Chapter- II LITERATURE SURVEY

2.1 THEORY OF BIODEGRADATION:

Market of LDPE, HDPE, PS and PP microfilms used in packaging carry bags is very wide. Many industrial units are based on the production of microfilms that are bioresistant. Hence legislation has been passed for the minimum film thickness that can be used for safe environment. It would be highly beneficial from the environmental and microfilm manufacturers stand point, if these films were biodegradable, decomposing almost completely under the attack of microorganism over a period of say few months or even they break into fragments so that they do not become harmful to the environment. (Rao K. J. et al 1996).

2.1.1 MODIFYING AGENTS

Various modifying agents are used with polymers to obtain certain specific properties. These modifiers are known to be microbial nutrients. This includes some lubricants and plasticizers. With the large number of destructive agents and the adaptability of each, it is highly probable that there are no plasticizers that are completely free from fungal or bacterial attack. Some are readily used by the microorganism as the source of carbon. As the microorganisms grow, they secrete digestive enzymes which accelerate the degradation process of the film by advancing the mycelial growth. The destruction of polymer by plasticizer results in tack and exudation, embrittlement, weight loss and discoloration. (Leonard I. Nass vol. I 1976).

2.1.2 PLASTICIZERS

Polyolefins in their unmodified form exhibit excellent resistance to biological destruction. When these polymers are compounded with additives or plasticizers the biological decomposition varies in degree and also is of various types. Plasticizers are substances that are added to plastic compounds to improve their flexibility, extensibility and processibility. Deterioration of the polymer by microorganisms is chemical, involving changes in composition and breaking of chemical bonds. It is the result of enzymes produced by the microorganisms. (P.D. Ritchie, 1972, Leonard I. Nass, vol. II 1976, H.F.Mark et alvol.2 1987).

2.1.3 THEORY OF PLASTICIZATION:

Plasticizers are occasionally used as processing aids in highly crosslinked polymers. Plasticizers appear to function in polar, mainly by masking polar sites in the chain and there by reducing hydrogen bonding. In all polymers, plasticizer tends to force the chain apart, giving them greater freedom of movement and also reducing van der Waals' forces between the chains. Thus there are no plasticizers that are completely free from fungal or bacterial attacks. Susceptibility of microbial attack increases as the plasticizer level increases. (Baboolal Agrawal series1968). There are three basic mechanisms for plasticizer loss: volatilization, extraction and microbiologic attack.

◊A plasticizer is a polymer additive that serves to increase the polymer's flexibility, elongation or ease of processing (workability). In more technical terms, the addition of a plasticizer generally causes a reduction in the cohesive intermolecular forces along the polymer chains. The chains can then move more freely relative to one another, and the stiffness of the polymer is reduced. (Cadogan, D F et al 1992,1996)

◊A good plasticizer should contain both polar and non-polar groups, the former ensure that the plasticizer is retained within the polymer and the latter attenuate the attractive forces between the polymer chains to give flexibility. The balance of polar and non-polar groups will determine its plasticizing performance. Smaller, more polar plasticizers will be more efficient and ensure ease of processing whereas larger, less polar and more linear molecules will confer better performance at extremes of temperature. (Ackley, David C 2000).

◊External Plasticizers, when added to a polymer, will cause the properties of elongation and softness of the polymer to be increased. It lowers the glass transition temperature, T_g, and reduces crystallinity by disrupting physical interactions between the chains. (Abbott, Barbara D 2000).

◊Plasticizer when incorporated in the polymer matrix is absorbed in the space between the polymer chains. They increase the free volume between the polymer chains. Thus the porosity of the polymer matrix is increased that help certain soil enzymes to attack the polymer. This reduces the van der Waals' forces between the chains and weakens the bonds between the monomers. Plasticizer is mixed with polymer. It penetrates and swells the polymer particles. Polar groups in the polymer are freed from each other. Polar groups of plasticizer interact with the polar groups of the polymer. The structure of the polymer is re-established, with full retention of plasticizer. (Carraher,et al 1996)

◊The plasticizer must have good physical interactions with high-molecular-weight polymers (Dominique Kay et al). This physical interaction causes the polymer and plasticizer to form a "homogenous physical unit." So that they do no separate out. Many polymers are not able to retain the plasticizer in the final product, leading to a product which is totally unacceptable. (Durodie, Bill July 2000).

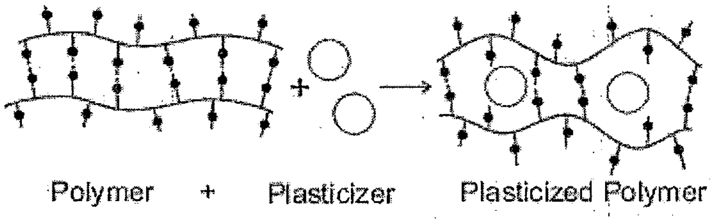

Figure: 2.1

Loss of Cohesion in polymer due to the absorption of solvent.

2.1.4 VARIOUS THEORIES TO EXPLAIN THE ACTION OF PLASTICIZERS:

There are many theories proposed to explain the action of plasticizers each having their short comings. Hence as on today there is no established theory that completely explains the action of plasticizer. (Brian Amato et al 2001)

2.1.4.a. The lubricity theory

This is based on the assumption that the rigidity of the resin arises from intermolecular friction binding the chains together in a rigid network. On heating these frictional forces are weakened so as to allow the plasticizer molecules between the chains. Once incorporated into the polymer bulk the plasticizer molecules shield the chains from each other, thus preventing the re-formation of the rigid network. Whilst attractive in its simplicity the theory does not explain the success of some plasticizers and the failure of others.

2.1.4.b. The gel theory

This extends the lubricity theory. The plasticizer breaks the resin-resin attachments and interactions by masking the centers of attachment from each other, preventing their reformation. It is insufficient to explain a completely plasticized system since while a certain concentration of plasticizer molecules will provide plasticization by this process the remainder will act more in accordance with the lubricity theory, with unattached plasticizer molecules swelling the gel and facilitating the movement of plasticizer molecules, thus imparting flexibility.

Molecules acting by this latter action may, on the basis of molecular size measurements, constitute the bulk of plasticizer molecules. If plasticization took place solely by this method it would not be possible to explain the ability of POLYMER resins to accept their own weight in plasticizer without exudation i.e. large amounts of additional space ("free volume") are created which other plasticizer molecules can occupy.

2.1.4.c. The free volume theory

This extends the above ideas and also allows a quantitative assessment of the plasticization process.

Free Volume of a polymer is described by the equation

Vf = Vt - V0

Where,

Vf = the free volume of the resin

Vt = specific volume at a temperature t

V0 = Specific volume of an arbitrary reference point, usually taken at zero degrees Kelvin

Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. A rigid resin (e.g. unplasticized polymer) is seen to possess very little free volume whereas resins which are flexible in their own right are seen as having relatively large amounts of free volume. Plasticizers therefore act so as to increase the free volume of the resin and also to ensure that free volume is maintained as the resin-plasticizer mixture is cooled from the melt. Combining these ideas with the gel and lubricity theories, it can be seen that plasticizer molecules not interacting with the polymer chain must simply fill free volume created by those molecules that do. These molecules may also be envisaged as providing a screening effect preventing interactions between neighboring polymer chains thus preventing the rigid polymer network reforming on cooling.

For the plasticized resin, free volume can arise from

◊Motion of the chain ends
◊Motion of the side chains and
◊Motion of the main chain

These motions can be increased in a variety of ways:

◊Increasing the number of end groups
◊Increasing the length of the side chain
◊Increasing the possibility of main group movement by the inclusion of segments of low static hindrance and low intermolecular attraction
◊Introduction of a lower molecular weight compound which imparts the above properties raising the temperature

The introduction of a plasticizer, which is a molecule of lower molecular weight than the resin, has the ability to impart a greater free volume per volume of material since there is an increase in the proportion of end groups. It has a glass transition temperature (Tg) lower than that of the resin itself. The use of a given plasticizer in a certain application will be a compromise between the above ideas and physical properties such as volatility, compatibility, high and low temperature performance, viscosity etc. (O'mara, Peggy 1999). This choice will be application dependent i.e. there is no ideal plasticizer for every application.

2.1.4.d. Solvation-desolvation equilibrium

Due to the observation of migration of plasticizer from plasticized polymers it is clear that at least some of plasticizer molecules are not bound permanently to the polymer as in an internally plasticized resin. An exchange/equilibrium mechanism is present. This implies that there is no stoichiometric relationship between polymer and plasticizer levels, although some quasi-stoichiometric relationships appear to exist.

2.1.4.e. Generalized structure theories and anti plasticization

The theories are based on the concept that if a small amount of plasticizer is incorporated into the polymer mass it imparts slightly more free volume and gives more opportunity for the movement of macro-molecules. Many resins tend to become more ordered and compact as existing "crystallites" grow or new "crystallites" form at the expense of the more fluid parts of the amorphous material. For small additions of plasticizer, the plasticizer molecules may be totally immobilized by attachment to the resin by various forces. These tend to restrict the freedom of small portions of the polymer molecule so necessary for the absorption of mechanical energy. Therefore it results in a more rigid resin with a higher tensile strength and base modulus than the base polymer itself. This phenomenon is therefore termed anti plasticization.

2.1.4.f. Specific interactions and interaction parameters

Early attempts to describe polymer-plasticizer compatibility were based on the same principles as used to describe solvation i.e. "like dissolves like". To obtain a quantitative measure of polymer -plasticizer compatibility a number of different parameters have been used. These are briefly described below.

2.1.4.g. The hilderbrand solubility parameter, d

This can be estimated based on data for a set of additive constants for the more common groups in organic molecules to account for the observed magnitude of the solubility parameter. These constants are designated F, for which

$d = F/V$

Where,

V = Molar volume.

2.1.4.h. Polarity parameters

These were evaluated by Van Veersen and Meulenberg and despite their apparent simplicity they show a good correlation with plasticizer activity for non-polymeric plasticizers. The parameter is defined as:-

$= M (Ap/Po) * 1000$

In which:

M = Molar Mass of Plasticizer

Ap = Number of Carbon atoms in the Plasticizer excluding Aromatic and Carboxylic Acid Carbon Atoms

Po = Number of Polar (e.g. carbonyl) groups present

The 1000 factor is used to produce values of a convenient number.

2.1.4.i. The solid-gel transition temperature, T_m

This is a measure of plasticizer activity. It is the temperature at which a single grain of polymer dissolves in excess plasticizer. The more efficient plasticizers will show lower values of T_m as a result of their higher solvating power. This can be correlated with the ease of processing of a given plasticizer, but all measurements should be conducted with a control polymer since clearly the choice of resin has an effect here also.

2.1.4.j. The flory-huggins interaction parameter

These ideas, based on a study of polymer miscibility, were applied to plasticizers by Anagnostopoulos according to the equation:-

$$1/ T_m = 0.002226 + 0.1351(1 -)/V1$$

Where,

V1 = Molar volume of the plasticizer, obtained from molar mass figures and density values at T_m

2.1.4.k. Recent summaries

The that solubility parameters were capable of classifying plasticizers of a given family in terms of their compatibility with polymer but they were of limited use for comparing plasticizers of different families (e.g. phthalates with adipates). Polarity parameters provided useful predictions of the activity of monomeric plasticizers but again were not able to compare activity of plasticizers from different families (Raloff, J. 2000). In all cases it was not possible to adequately predict the behavior of polymeric plasticizers.

2.1.4.l. Specific interactions

Some mechanism of attraction and interaction between polymer and plasticizer must exist for plasticizer to be retained in the polymer after processing.

2.1.4.m. Molecular modeling

A range of plasticizer molecule models highlighted the free volume increase caused by the mobility of the plasticizer alkyl chains. More detailed models concentrating on the polar region of the plasticizer and its possible mode of interaction with the polymer showed the expected repulsion between areas on the polymer and plasticizer of like charge as well as attraction between the negative portions of the plasticizer and positive portions of the polymer. (Byungtae Lee et al 1991).

It can be concluded from all of these theories and studies that plasticizer polarity is important in determining the gelation rate of the plasticizer but it does not explain other properties of interest in the final product. The conformation adopted by plasticizer molecules in the polymer matrix in the final product is important, since this will relate to the number of polymer-polymer chain-chain interactions are screened from each other and the amount of free volume created. (T. D. Stark et al 2005). The recent studies have shown that this conformation is not so important in samples which have experienced high processing temperatures, since in these samples the separation of the polymer chains, and ingress of plasticizer, is controlled more by thermal energy than by plasticizer polarity. At lower processing temperatures the polarity of the plasticizer has a greater role in the attainment of acceptable physical properties of the final product.

2.1.5 PLASTICIZERS SUSCEPTIBLE TO MICROBIAL ATTACK

Plasticizers possess low melting point, elastic modulus, melt viscosity and second order transition temperature. They do not alter the chemical nature of the macromolecules of the polymer. They are commonly used in linear, branched and highly crosslinked polymer. They appear to function in polar polymer, mainly by masking the polar sites in the chain and thereby reducing hydrogen bonding. They tend to pull the chains apart, giving them greater freedom of movement by reducing the van der Waals' forces. They reduce the hardness, increase the extensibility and improve the susceptibility towards the microbial attack. (Audic, J.L. 2005). Various plasticizers that exhibit higher susceptibility towards microbial attack are: acetals, butyrates, laurates, oleates, sebacates, epoxidized oil, epoxidized tallate esters, polyester, glycolates, stearates, abiotic acid derivatives, aliphatic acid derivatives, aliphatic alcohols, n-phthalic acid derivatives, rcinoleates, succinic acid derivatives. Vegetable oils like tung oil, linseed oil, soy been oil, cottonseed oil, castor oil, dehydrated castor oil, ground nut oil, etc, also exhibit higher susceptibility towards microbial attack. (Leonard I. Nass, vol. II 1976, Mark et alvol.2 1987).

2.1.6 MICROORGANISMS

The microorganisms associated with degradation of polymer belong to different groups of fungi and bacteria. The fungal deterioration is most effective because they cause discoloration, change in odor, loss of weight, embrittlement, exudation, loss of strength, changes in electrical properties. Certain organisms produce colored metabolic by products that are soluble in plasticized polymer and readily migrate in to and through the polymer. Bacterial attack is similar to fungal attack, but they survive in aerobic or anaerobic environments, deep in the soil or in the deoxygenated water. Bacteria cause shrinkage, stiffening, discoloration and loss of electrical resistivity. (Huijberts GNM, et al 1992). Various fungi used to study biodegradation are: (Leonard I. Nass, vol. II 1976, Mark et alvol.2 1987).

1. Alternaria tenuis,
2. Aspergillus flavus,
3. Aspergillus niger,
4. Aspergillus oryzae,
5. Cladosporium herbarum,
6. Curvularia geniculata,
7. Fusarium sp.,
8. Glomerella cingulata,
9. Mucor sp.,
10. Myrothecium verrucaria,
11. Paecilomyces varioti,
12. Penicilium funiculosum,

13. Penicillium luteum,
14. Penicillium piscarium,
15. Pulluvia pullulans,
16. Rhizopus.
17. Stachybotrys atra.
18. Stephylium consortiale,
19. Trichoderma viride,

Various Bacteria used (Steinbüchel A et al 1998) to study biodegradation are:

1. Bacillus subtilis,
2. Escheritia coli,
3. Pseudomonas aeruginosa,
4. Serratia marcescens,
5. Staphylococcus aureus,
6. streptomyces rubrireticuli

2.1.7 THE BIOLOGICAL SYSTEM:

The degradation of polymer occur by different molecular mechanisms; chemical-, thermal-, photo and bio-degradation. Biodegradation is defined as any physical or chemical change in a material caused by any environmental factor, including light, heat, moisture, wind, chemical conditions or biological activity. The biodegradation of plastics proceeds actively under different soil conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the soil. (J. E. Glass, et al 1989). Thus in a given span of time all materials biodegrade when they are subjected to suitable biological system. Degradation mechanisms of polymers are different from one other depending on their molecular structure and specific formulation (additives, pigments, etc.) the chemical composition of polymer chains will determine the families of physical and chemical degradation mechanisms likely to take place into the material. Other important material's characteristics which can influence the finished product's sensitivity:

◊Polymer chain's structure (level of linearity, branching, cross-linking);

◊Molecular weight distribution (can be illustrated as the distribution in length of polymer chains in the material)

◊Morphology (polymer chains relative orientation, crystallinity, etc.)

◊Irregularities (structural irregularities, impurities, traces of catalysts, etc.)

◊-Additives (antioxidants, UV stabilizers, pigments, charges, plasticizers, etc.) (Yüksel Orhan 2004)

Thermal and shear stresses sustained by the material during processing can initiate degradation mechanisms (thermal degradation, hydrolysis, etc.), sensitize the material to some other mechanisms (formation of sensitizing structures, degradation or bad mixing of stabilizers, etc.) and control the final morphology of the material (chain orientation, crystallinity, internal stress, etc.). Every polymer has its own field of sensitivity. Some environments have no significant impact on some polymer, while they can have a high impact on other materials properties. Degradation can arise in specific exposure conditions only, but not in common fields of practice. The key parameters to be considered with regard to long-term degradation include temperature, moisture, UV radiation, thermal stress, chemical environment, mechanical stress, microbiological activity and atmospheric pollution. Physical aging is related to degradations which do not involve a modification in the molecular structure of polymer chains. Some of these mechanisms involve a mass transfer with the environment surrounding the material (extraction of additive, absorption of solvent, etc.). Others involve a modification of internal chain organization into the material, i.e. a change of morphology (chain orientation, crystallinity, etc.). The main physical degradation mechanisms likely to influence the performance of materials are Additive extraction. Different types of additives i.e. antioxidants, UV stabilizers, pigments, plasticizers, fillers, etc when exposed to some particular conditions can lead to a partial or total extraction of the additives from the material. Additives can be leached at the surface of the material by water or any other chemical agent in contact. Some volatile additives can also evaporate, i.e. plasticizers. If the rate of diffusion of the additive from the bulk to the surface is slow compared to the rate of extraction and/or consumption at the surface, the concentration of the additive at the surface decreases and a concentration profile is built into the material. If this additive is involved in a stabilization process, the level of protection at the surface can be altered, which can eventually lead to the onset of local degradation, even if the concentration of that additive in the bulk remains high. (Dominique Kay et al,)

◊The material contains additives which have a low level of solubility in the polymer and/or are highly volatile

◊The material will be in contact with a solvent susceptible to have a high level of interaction with an additive

◊The material will be exposed to high temperature (high temperature favoring the migration of additives to the surface by increasing molecular chains' mobility).

A high interaction of solvent-polymer favors the penetration of solvent molecules into the material. These molecules break the interactions between polymer chains, increasing the distance between them and reducing their cohesion, which increases their mobility. This typically leads to an increase in dimensions (swell) and a loss of stiffness. But solvent absorption can also lead to irreversible degradation mechanisms such as loss of shorter polymer chains, crazing and hydrolysis. In some cases, absorption of a solvent can lead to the formation of cracks by a process called crazing. This mechanism consists in the propagation of a crack associated to the alignment of molecular chains in the stress direction (disentanglement of the chains).

A biological system comprises of microorganism/s, the environmental factors such as temperature, pressure, relative humidity, methods of handling/storage, presence/absence of oxygen, the material, the molecular weight, crystallinity, cross linking, branching, copolymerization, plasticization, orientation, and residual stresses of the material, the volume, and the contact area to various environmental conditions.

This can be explained by various examples observed in our daily routine:

◊An oil contaminated rubber band when subjected to atmospheric conditions, loses its properties and strength, and becomes tacky after certain period. On the other hand an oil seal made of rubber do not lose its property even after number of years of service.

◊Tightly rolled news papers were found to be intact and entirely legible after forty years' burial in local dumps (I. Luis Gomez, 1990) which or otherwise are known to be biodegradable in short time.

◊Many articles like house wares, toys, ornaments etc. of ancient times are obtained in tact during the archeological digging.

◊Iron and other such metals do not decompose until suitable environmental exposure is available.

◊The blood clots when exposed to the oxygen in air, but not when exposed to the oxygen within the body which it conveys in the whole body.

From the above examples and many other such examples where a particular material exhibit unusual properties in certain environmental conditions can be explained by the existence of a biological system.

It would be very interesting to identify such biological system. If such biological system could be identified for all material then the service life of the material can be regulated as per the requirement of the user.

2.2 TEST METHODS TO ASSESS BIODEGRADABILITY OF POLYMERS:

Enormous work is being carried out in the field of biodegradable polymers. Hence the researchers must be aware of the Standard Test methods available for the measurement of the degree of degradation. A range of International Standards, and Test methods are developed specifically for biodegradability. Laboratory test protocols are usually evaluation of environmental degradation under simulated conditions to which a particular polymer will be exposed on disposal. (Progelhof R. C. 1986). Correlation with real world exposure is more difficult for biodegradation than photo degradation because the environment for biodegradation widely differ in microbial composition, pH, temperature, moisture, etc. hence can not be readily reproduced. In early years, the only tests to establish biodegradability were related to the microbial growth, weight loss, tensile and other physical properties losses. These all are indirect measurements of biodegradation often leads to results that are difficult to reproduce from laboratory to laboratory, giving rise to confusion on the susceptibility to biodegradation of a given polymer.(Rubin, Irvin I., et al. 1998.)

2.2.1 STANDARD ORGANISATIONS FOR TESTING:

There are number of International Standards, and Test methods, developed specifically for biodegradability, product safety, and also for compost derived products. (R. P. Brown 1981, Vishu Shah 1998). The main International Organizations that have established standards or testing methods are:

◊American Society for Testing and Materials (ASTM) (www.astm.org); (ASTM D 638, 1980).

◊European Standardization Committee (CEN) (www.cenorm.be);

◊International Standards Organization (ISO) (www.iso.org);

◊Institute for Standards Research (ISR),

◊German Institute for Standardization (DIN); and

◊Organic Reclamation and Composting Association (ORCA) (Belgium).

2.2.2 AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) METHODS

ASTM D6692-01: Standard Test Method for Determining the Biodegradability of Radio labeled POLYMERIC Plastic Materials in

Seawater. This test is used to determine the degree of aerobic biodegradation of polymeric compounds utilized in plastic materials by determining the level of respiration of such radio labeled carbon compounds to radio labeled carbon dioxide.

◊**ASTM D6954-04:** Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation. It is used to compare and rank the controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal, photo oxidation processes and the biodegradation.

◊**ASTM D6691-01:** Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium. It is used to determine the degree and rate of aerobic biodegradation of plastic materials (including formulation additives) exposed to at least ten aerobic marine microorganisms of known genera. The test method is conducted under controlled laboratory conditions.

◊**ASTM D6002-96(2002):** Standard Guide for Assessing the Compostability of Environmentally Degradable Plastics. It covers suggested criteria, procedures, and a general approach to establish the compostability of environmentally degradable plastics.

◊**ASTM D6340-98(2007):** Standard Test Methods for Determining Aerobic Biodegradation of Radiolabeled Plastic Materials in an Aqueous or Compost Environment. These test methods directly determine the rate and degree of biological oxidation of carbon in plastic materials when placed in a composting environment containing simulated municipal solid waste or an aqueous environment under laboratory conditions.

◊**ASTM D5271-02:** Standard Test Method for Determining the Aerobic Biodegradation of Plastic Materials in an Activated-Sludge-

Wastewater-Treatment System. This test method indexes plastic materials which are more or less biodegradable relative to a standard in aerobic activated-sludge-treatment systems.

◊**ASTM D5209-92:** Standard Test Method for Determining the Aerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge (Withdrawn 2004). In this test method the degree and rate of aerobic biodegradation of synthetic plastic materials (including formulation additives that may be biodegradable) on exposure to activated-sewage sludge inoculum under laboratory conditions is measured.

◊**ASTM D5951-96(2002):** Standard Practice for Preparing Residual Solids Obtained After Biodegradability Standard Methods for Plastics in Solid Waste for Toxicity and Compost Quality Testing. It is a standard procedure for preparing the residual solids obtained at the end of standard methods for biodegradability testing of plastics in solid waste, for subsequent toxicity and compost quality testing.

◊**ASTM D5338-98(2003):** Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions. In this test method the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled-composting environment under laboratory conditions is determined.

◊**ASTM D6400-04:** Standard Specification for Compostable Plastics. This specification mentions that if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials.

◊**ASTM D7081-05:** Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment. This specification determines that if products made from plastics (including packaging and coatings) are designed to be biodegradable under the marine environmental conditions of aerobic marine waters or anaerobic marine sediments, or both, will biodegrade satisfactorily. Further, it assures that the degradation of these materials will not diminish the value or utility of the marine resources and habitat.

◊**ASTM D6954-04:** Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation. This test compares and ranks the controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal, photo oxidation processes, the biodegradation and ecological impacts in defined applications and disposal environments after degradation. Disposal environments range from exposure in soil, landfill, and compost.

◊**ASTM D6868-03**: Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates. This specification states that the biodegradable plastics and products (including packaging), where plastic film or sheet is attached (either through lamination or extrusion directly onto the paper) to substrates and the entire product or package will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. Also the properties will assure that the degradation of these materials will not diminish the value or utility of the compost resulting from the composting process.

◊**ASTM D6094-97(2004):** Standard Guide to Assess the Compostability of Environmentally Degradable Nonwoven Fabrics. In this test method the criteria, procedures, and a general approach to establish the compostability of environmentally degradable nonwoven fabrics and products is covered.

◊**ASTM D5509-96:** Standard Practice for Exposing Plastics to a Simulated Compost Environment (Withdrawn 2002). In this test the exposure of plastics to a specific test environment is covered. The test environment is a laboratory-scale reactor that simulates a self-heating composting system and that uses aeration to control maximum temperature. Plastic is exposed to a media undergoing aerobic composting. The standard media simulates a municipal solid waste.

◊ **ASTM D5512-96:** Standard Practice for Exposing Plastics to a Simulated Compost Environment Using an Externally Heated Reactor (Withdrawn 2002). The test environment employed here is an externally-heated laboratory-scale reactor that simulates a composting system using standard media that simulates a municipal solid waste from which inert materials have been removed. Further testing of specimens is made for comparison with controls.

◊ **ASTM D6003-96:** Standard Test Method for Determining Weight Loss From Plastic Materials Exposed to Simulated Municipal Solid-Waste (MSW) Aerobic Compost Environment (Withdrawn 2005). This test method was used to determine the degree and rate of aerobic biodegradation of plastic materials exposed to a controlled composting environment. Aerobic composting takes place in an environment where temperature, aeration, and humidity are closely monitored and controlled.

◊ **ASTM D5510-94(2001):** Standard Practice for Heat Aging of Oxidatively Degradable Plastics. This test defines the exposure conditions of plastics at various temperatures when exposed solely to hot air for extended periods of time. Only the procedures for heat exposure are specified, not the test method or specimen.

◊ **ASTM D5988-03:** Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting. This test method determines the degree and rate of aerobic biodegradation of synthetic plastic materials (including formulation additives that may be biodegradable) in contact with soil, or a mixture of soil and mature compost, under laboratory conditions.

◊ **ASTM D5247-92:** Standard Test Method for Determining the Aerobic Biodegradability of Degradable Plastics by Specific Microorganisms

(Withdrawn 2004). In this test method the procedures required to carry out a pure-culture study for evaluating the biodegradation of degradable plastics in submerged culture under aerobic conditions is described. Degradation is evaluated by weight loss, tensile strength loss, percent-elongation loss and changes in molecular-weight distribution.

◊**ASTM D5437-93:** Practice for Weathering of Plastics under Marine Floating Exposure (Withdrawn 1999). Here the experimental conditions for exposure of plastics to marine environments, outdoor brackish water and fresh-water exposures are mentioned.

◊**ASTM D5525-94a:** Standard Practice for Exposing Plastics to a Simulated Active Landfill Environment (Withdrawn 2002). Here the plastics are exposed to a specific test environment where a laboratory-scale reactor that simulates a landfill with enhanced biological activity is used. Biological activity is enhanced by adding moisture, recirculation of leachate, and heating to 35°C.

◊**ASTM D5526-94(2002):** Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials under Accelerated Landfill Conditions. This test method determines the degree and rate of anaerobic biodegradation of plastic materials and mixtures of household waste in an accelerated-landfill test environment.

◊**WK9579 Revision of ASTM D5526-94(2002):** Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions D5526-94(2002)Developed by Subcommittee: D20.96. It measures the degree of degradation / disintegration in the aerobic phase over time which correlates with the packing of landfill sites and volume availability.

◊**ASTM D5511-02:** Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials under High-Solids Anaerobic-Digestion Conditions. It determines the degree and rate of anaerobic biodegradation of plastic materials in high-solids anaerobic conditions. The test materials are exposed to a methanogenic inoculum derived from anaerobic digesters operating only on pretreated household waste. The anaerobic decomposition takes place under high-solids (more than 30 % total solids) and static non-mixed conditions.

◊**ASTM D5210-92(2000):** Standard Test Method for Determining the Anaerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge. It determines the degree and rate of anaerobic biodegradation of synthetic plastic materials (including formulation additives) on exposure to anaerobic-digester municipal sewage sludge from a waste-water plant, under laboratory conditions.

◊**ASTM D3826-98(2002):** Standard Practice for Determining Degradation End Point in Degradable Polyethylene and Polypropylene Using a Tensile Test. This test determines a degradation-end point *(a brittle point)* for degradable polyethylene/polypropylene films and sheeting less than 1.0 mm (0.04 in.) thick.

◊**ASTM D5272-92(1999):** Standard Practice for Outdoor Exposure Testing of Photodegradable Plastics. This test defines test conditions applicable when Practices D1435 and G7 are employed for the outdoor exposure testing of photodegradable plastics.

◊**ASTM D5071-06:** Standard Practice for Exposure of Photodegradable Plastics in a Xenon Arc Apparatus. In this test the specific procedures, the preparation of test specimens, and test conditions that are applicable for xenon arc exposure of photodegradable plastics conducted in accordance with Practices G 151 and G 155 is mentioned. It also covers the test conditions best suited for photodegradable plastics, and the evaluation of test results.

◊**ASTM D5208-01:** Standard Practice for Fluorescent Ultraviolet (UV) Exposure of Photodegradable Plastics. In this test the specific procedures applicable, the preparation of test specimens and the evaluation of test results for fluorescent Ultraviolet (UV) exposure of photodegradable plastics conducted in accordance with Practices G 151 and G 154 is covered.

2.2.3 GROWTH RATINGS G-21-70 AND GZZ-76:

In these test the resistance of plastics to fungal and bacterial growth is assessed. Fungi like aspergillus niger, pennicillium at 28-30°C temperature at 85% RH for 21 days is used. Bacteria like pseudomonas aeruginosa incubated at 35-57°C for minimum 21 days are used. After suitable time the growth is assessed in terms of % surface covered. The test gives quick results. It is easy to do and give indication of biodegradation. But it is not conclusive for biodegradation of polymer. (ASTM G21-70, 1980).

2.2.4 International Standards Organization (ISO): (WWW.ISO.ORG) European biodegradable plastics are currently assessed by ISO 14855, which is a controlled aerobic composting test and ISO 14851 and ISO 14852 are biodegradability tests specifically designed for polymeric materials.

2.2.5 ISO 846 (1978): It specifies the use of a mixture five strains of fungi over a period of at least 28 days at 30 ±2°C and 95-100% RH. The results of attack are measured by visual examination for growth. Method A is used to determine the ability of plastics to act as the carbon and nitrogen source for the growth of microorganisms. Method B is used to determine the fungi toxic properties of plastics.

2.2.6 COMPOST TOXICITY TESTS: For a comprehensive assessment of toxicity associated with compost applications, plastics can be tested on both plant and animal species. A number of polyester types were tested including a plasticized cellulose acetate, an aliphatic polyester, polyhydroxybutyrate-co-hydroxyvalerate and polycaprolactone. Cell culture medium with serum was used as the extraction medium. (Nolan-ITU *2002* Last updated 2007).

2.2.7 PLANT PHYTOTOXICITY TESTING: While a product may not negatively impact plant growth in the short term, over time it could become phytotoxic due to the build-up of inorganic materials, which could potentially lead to a reduction in soil productivity. For this reason some manufacturers use plant phytotoxicity testing on the finished compost that contains degraded polymers. Phytotoxicity testing can be conducted on two classes of flowering plants. These are monocots (plants with one seed leaf) and dicots (plants having leaf with two seeds). Representatives from both of these classes are typically used in toxicity testing - summer barley to represent monocots and cress to represent dicots. Tests involve measuring the yield of both of these plants obtained from the test compost and from control compost. (Nolan-ITU *2002* Last updated 2007).

2.2.8 ANIMAL TOXICITY TEST: Animal testing is generally carried out using earthworms (as representative soil dwelling organisms) and Daphnia (as representative aquatic organisms). Earthworms are very sensitive to toxicants. Since earthworm feeds on soil, they are suitable for testing the toxicity of compost. In the acute toxicity test, earthworms are exposed to high concentrations of the test material for short periods of time. Earthworms are exposed to soil and compost in varying amounts. Following 14 days of exposure, the number of surviving earthworms is counted and weighed and the percent survival rate is calculated. The earthworms are exposed to several mixture ratios of compost and soil mixtures. Compost worms are used for testing the toxicity of biodegradable plastic residues. These worms are very sensitive to metals such as tin, zinc, and heavy metals and high acidity. For this test worms are cleaned and accurately weighed at intervals over 28 days. The compost worm toxicity test is considered to be an accurate method. The toxicity test can establish whether degradation products present in liquids pose any problem to surface water bodies. In the test, Daphnia are placed in test solutions for 24 hours. After exposure the number of surviving organisms is counted and the percent mortality is calculated. (Nolan-ITU *2002* Last updated 2007).

2.2.9 SOIL BURIAL TEST BS 4618 SEC.4.5 1974: Soil burial is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. It lacks reproducibility because of the difficulties in controlling climatic factors and the population of various biological systems that are involved. Generally the samples are buried in soil for periods of up to two years. At the end of the resting period, changes in properties like loss in weight, mechanical strength, shape etc. are studied. It provides qualitative indication of biodegradation.

2.2.10 DIFFERENCE BETWEEN STANDARDS FOR BIODEGRADATION: The main point of differentiation between the various international standards is the percentage of biodegradation required for compliance. This is an important issue that is under discussion at ISO level. (Nolan-ITU *2002* Last updated 2007).

Table 2.1 - Standards Compliance Requirements

Standard	Biodegradation Requirement
DIN	60% 6 MONTHS
ASTM	60% 6 MONTHS
CEN	90% No specific time is mentioned
OECD	60% 28 days

2.3 CLASSIFICATION OF BIODEGRADABLE POLYMERS:

Today polymer industry is facing environmental problems. Most of the polymer does not degrade under standard environmental conditions. Some polymers however degrade in biological environment. By increasing their use the environmental problems can be resolved to a certain extent. (Goldstein N. et al 2000.)

Biodegradable polymers can be divided into three broad classifications:

- ◊Natural polymers or biopolymers
- ◊Synthetic polymers: (a) Carbon chain backbone (b) Heteroatom chain backbones
- ◊Modified Natural polymers: Blends and grafts, Chemically modified, Oxidation and Esterification (Kohudic, et al 1998).

2.3.1 NATURAL POLYMERS OR BIOPOLYMERS:

They are produced naturally by all living organisms. (Kim B. S., et al 1992, 1994). They are environmentally acceptable degradable polymers. Most common natural polymers are:

1. Polysaccharides: starch and cellulose
2. Proteins: silk and poly (2-Glutamic acid)
3. Polyesters: polyhydroxyalkanoates (Hasirci, V. 2000).

2.3.2 SYNTHETIC POLYMERS:

Synthetic polymers do not have natural origin; the enzymes available in nature for degrading natural polymers are not useful for synthetic polymers. Studies were carried out for synthetic polymeric structure that can be biodegraded. (Gage P.1990). Some guidelines based on polymer structure, polymer physical properties and environmental conditions at the exposure sites emerged for polymer structures. (Zuchowska D., et al 1998). Following generalization can be made:

- ◊A higher hydrophilic/hydrophobic ration is better for degradation.
- ◊Carbon chain polymers are unlikely to biodegrade.
- ◊Chain branching is deleterious to biodegradation.
- ◊Condensation polymerization is more unlikely to biodegrade.
- ◊Lower molecular weight polymers are more susceptible to biodegradation.
- ◊Crystallinity reduces biodegradability.

Favorable polymer physical properties include water solubility and sample purity. Environmental conditions to be considered in evaluation of biodegradability are temperature, pH, moisture, oxygen, nutrients, suitable microbial population, and concentration and test duration. (Davis G., 2003).

POLYMERS WITH CARBON BACKBONES:

These polymers may be represented by and is considered derivatives of $-$ (-R-CH-) $-_n$. Where 'n' is the degree of polymerization and 'R' is the functional group. The functional groups and the molecular weight of the polymer control their properties that vary in hydrophobicity, solubility characteristics, Tg and crystalinity. (Hocking PJ, et al 1994).

HETERO ATOM CHAIN BACKBONE POLYMERS:

Their linkages are quite frequently found in nature and they are more likely to biodegrade than hydrocarbon based polymers. They include polyesters, polyamides, polyethers, polyacetates and other condensation polymers. (Huang J. C., et al 1990).

2.3.3 MODIFIED NATURAL POLYMERS:

Natural polymers can also be modified so that the environmentally acceptable polymer can be developed. Also the modification should not retard the biodegradation process. (Dr. Joseph P. Greene 2005). The modification includes blends with other natural and synthetic polymers, grafting of other polymeric composition and chemical modification to introduce some desirable functional group by oxidation or some other simple chemical reaction such as esterification or etherification. (Jennifer Farrin 2003).

2.3.4 NATURALLY PRODUCED POLYMERS:

Following naturally produced biodegradable polyesters are under development for commercialization.

Table: 2.2 Biodegradable polyesters in commercial development (Fritzsche K, 1990).

PHA	polyhydroxyalkanoates
PHB	polyhydroxybutyrate
PHH	polyhydroxyhexanoate
PHV	polyhydroxyvalerate
PLA	polylactic acid
PCL	polycaprolactone
PBS	polybutylene succinate
PBSA	polybutylene succinate adipate
AAC	Aliphatic-Aromatic copolyesters
PET	polyethylene terephthalate
PBAT	polybutylene adipate/terephthalate
PTMAT	Polymethylene adipate/terephthalate
PGA	polyglycolic acid
PLLA	poly (L- lactic acid)

2.4 COMMERCIALLY AVAILABLE BIODEGRADABLE POLYMERS:

2.4.1 POLY ETHER KETONE (PEK)

Controlled chemical oxidation of PVA_L results into PEK. PEK is found more susceptible to hydrolysis and biodegradation than PVA_L. Its water solubility, reactivity and biodegradability make it potentially useful material in biomedical, agricultural and water treatment areas. PEK and PCL blends are excellent controlled release systems. (Hollinger J O 1995)

2.4.2 MODIFIED PET

Modified PET (polyethylene terephathalate) is PET which contains co-monomers, such as ether, amide or aliphatic monomers, that provide 'weak' linkages that are susceptible to biodegradation through hydrolysis. Modified PET materials include PBAT (polybutylene adipate/terephthalate) and PTMAT (polytetramethylene adipate/terephthalate). Modified PET is hydro-biodegradable. Weak linkages create sites for microbial attack. Hydrolysis of the ester linkages and enzymatic attack on ether and amide bonds take place. (R. Dvorak and E. Kosior, 2000).

2.4.3 POLYACRYLATE

Polyalkyl acrylates and polycyanoacrylates generally resist biodegradation. Weight loss in soil burial test is reported for copolymers of ethylene and propylene with acrylic acid, acrylonitirde and acrylamide poly alkyl 2-cyanoacrylates. Polymethyl 2-cyanoacrylate is the most degradable among the esters. The degradability decreases as the alkyl size increases. It swells in water to form a hydrogel and is widely used in biomedical area due to its good biocompatibility. (Hayashi T 1994).

2.4.4 POLYAMIDE ENAMINES

Homogeneous erosion of hydrophilic biodegradable polymer matrix system undergoes progressive loosening or swelling. Hence by surface erosion, a near zero order release can be obtained if diffusion release is small. Poly [amide-enamine]s are are found susceptible to hydrolysis and biodegradation. (Potts J.E., 1981 Nolan-ITU *2002* Last updated 2007).

2.4.5 POLYAMIDES

Nylon 6, Nylon 6, 6 generally resist microbial and enzymatic attacks but oligomers of e-amino hexanoic acid are degraded by enzymes and microorganism. The loss of tensile strength of nylon in vivo is by 25% after 89 days and 83% after 726 days. Etching of a nylon fiber after 210 days in vivo is also seen. (Lewis OG, et al 1997). In vivo degradation of nylon is caused by hydrolysis and proteolytic enzyme catalysis. Incorporation of methyl, hydroxy and benzyl groups into polyamide chains improves the biodegradability. Biodegradability of polyamide esters decreases by shortening polyamide blocks and increasing polyamide content.

2.4.6 POLYANHYDRIDES

Polyanhydrides degrades by surface erosion. Polyanhydrides degrade by hydrolysis of the anhydride linkage. The hydrolytic degradation rates can be altered by simple changes in the polymer backbone structure by choosing the appropriate diacid monomers. (Burkoth AK, 2000). Poly (sebasic acid) degrades quickly (about 54 days in saline), while poly(1,6-bis(-*p*-carboxyphenoxy)hexane degrade much more slowly (estimated 1 year). Their main applications are in controlled drug delivery. (Domb AJ, et al 1994). Polyanhydrides are synthesized by dehydration of the diacid or a mixture of diacids by melt polycondensation. The dicarboxylic acid monomers are converted to the mixed anhydride of acetic acid by reflux in excess acetic anhydride. High molecular weight polymers are prepared by melt-polycondensation of prepolymer in vacuum under nitrogen sweep. Domb AJ, et al 1987). Polyanhydrides have limited mechanical properties that restrict their use in load-bearing applications such as in orthopaedics. To combine good mechanical properties of polyimides with surface-eroding characteristics of polanhydrides, poly (anhydrides-co-imides) have been developed for orthopaedic applications. (Attawia MA, 1995, John C. Middleton et al 2003).

2.4.7 POLYDIOXANONE (POLYETHER ESTER)

The ring-opening polymerization of *p*-dioxanone resulted in PDS. This material has 55% crystallinity, glass-transition temperature of −10 to 0°C. The polymer should be processed at the lowest possible temperature. The monofilament loses 50% of its initial breaking strength after 3 weeks and is absorbed within 6 months. (Jen AC, et al 1999).

2.4.8 POLYESTERS:

They are biodegradable, can be processed as plastic materials, are produced from renewable resources and can be produced by many bacteria in a range of composition. The thermoplastic polymers vary from soft elastomer to rigid brittle plastics. All the polyesters are 100% optically pure and are 100% isotactic. Elastomeric polyesters have excellent toughness and strength and are inherently biodegradable. But as the chain length increases the rate of biodegradation is greatly reduced. Aliphatic polyesters are the most easily biodegraded synthetic polymers known. (Amass W, Amass A, Tighe B 1998).

2.4.8.a. PLA

Polylactic acid (PLA) is linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group. (Mikos A.G, et al 1994). Lactic acid is produced (via starch fermentation) as a co-product of corn wet milling. The ester linkages in PLA are sensitive to both chemical hydrolysis and enzymatic chain cleavage. (Gogolewski S, et al 1983). PLA is often blended with starch to increase biodegradability and reduce costs. However, the brittleness of the starch-PLA blend is a major drawback in many applications. (Cutright D, et al 1971). To remedy this limitation, a number of low molecular weight plasticisers such as glycerol, sorbitol and triethyl citrate are used. The material has good rigidity characteristics, allowing it to replace polystryene and PET in some applications. (Bergsma JE, et al 1995).

2.4.8.b. PGA

Polyglycolide is the simplest linear aliphatic polyester. Glycolide monomer is synthesized from the dimerization of glycolic acid. Ring-opening polymerization yields high-molecular-weight materials. Poly (glycolic acid) (PGA) is a rigid thermoplastic material with high crystallinity(46-50%). The glass transition and melting temperatures of PGA are 36 and 225°C, respectively. Common processing techniques such as extrusion, injection and compression moulding can be used to fabricate PGA but it requires careful control of processing conditions. Its degradation product glycolic acid is a natural metabolite. A major application of PGA is in resorbable sutures. (Chu CC 1981 a, b, c). Sutures of PGA lose about 50% of their strength after 2 weeks and 100% at 4 weeks, and are completely absorbed in 4—6 months. (Böstman O, et al 1992, 1992b). Poly (lactic-glycolic acid) (PLGA) is copolymer of PGA.) LA/GA is amorphous and resistance to hydrolysis is more. The 70/30 GA/LA has the highest water uptake. (Ashammakhi N, et al 1997)

2.4.8.c. PHA

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters naturally produced via a microbial process on sugar-based medium, where they act as carbon and energy storage material in bacteria. (Doi Y, Tamaki A et al 1988, Doi Y, Abe C et al 1990, Doi Y, Kawaguchi Y et al 1992). PHA family comprises of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). (Amos DA, et al 1989). Such polymers are actually synthesized by microbes, (Holmes PA 1988) with the polymer accumulating in the microbes' cells during growth. (Anderson AJ, et al 1990, Haywood GW et al 1991). The PHB homo polymer is a stiff and rather brittle polymer of high crystallinity, whose mechanical properties are not unlike those of polystyrene, though it is less brittle. PHAs are biodegradable via composting. (Abe H, Doi Y, 1994, Byrom D 1994).

2.4.8.d. PHB/PHV

PHB/PHV is a copolymer of PHA which incorporates plasticizer/softener and inorganic additives such as titanium dioxide and calcium carbonate. (Baptist JN 1962, Byrom D 1992).

2.4.8.e. PBS

Polybutylene succinate (PBS) is biodegradable synthetic aliphatic polyester with similar properties to PET. PBS is generally blended with other compounds, such as starch (TPS) and adipate copolymers (to form PBS-A), to make its use economical. PBS has excellent mechanical properties. Applications include mulch film, packaging film, bags and 'flushable' hygiene products. PBS is hydro-biodegradable and begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages which results in a lowering of the polymer's molecular weight, allowing for further degradation by micro-organisms. (Nolan-ITU *2002* Last updated2007).

2.4.8.f. PCL

Polycaprolactone (PCL) is biodegradable synthetic aliphatic polyester made by the ring-opening polymerization of caprolactone. PCL has a low melting-point, between 58-60°C, low viscosity and is easy to process. Cost barriers have been overcome by blending the PCL with corn-starch. (Koleske J V 1978). PCL without additives completely degraded after six weeks in compost with activated sludge. The introduction of processing additives gave better tensile strength of the materials but made them less vulnerable to micro-organism attack. After eight weeks, the PCL in seawater was completely decomposed, whereas that in salt solution had lost only 20% of its weight. The tensile strength, in buffered salt solution had decreased to one-sixth its original value. (Janik, H., et al 1998).

2.4.8.g. PPF

The degradation of polyesters based on fumaric acid leads to fumaric acid, a naturally occurring substance. The copolymer has unsaturated sites in its backbone. The copolymers degrade to propylene glycol, poly (acrylic acidco-fumaric acid) and fumaric acid. Cross-linking occurs with methylmethacrylate or N-vinyl pyrolidone and benzoyl peroxide as the initiator. Achieving high molecular weight PPF is difficult because of side reactions, particularly due to the presence of the backbone double bond. hence fillers of ceramic materials such as tricalcium phosphate (TCP), calcium carbonate or calcium sulfate are added, or further reactions to form cross linked net works is carried out to achieve good mechanical strength. The mechanical properties depend on the method of synthesis and the cross-linking agent used. PPF undergoes bulk degradation and degradation time is dependent on polymer structure and other components. PPF degrades by hydrolysis to fumaric acid and propylene glycol. The time required to reach 20% loss in original weight ranged from 84 - 200 days. (Kharas GB, et al 1997).

2.4.8.h. AAC

Aliphatic-aromatic (AAC) copolyesters combine the biodegradable properties of aliphatic polyesters with the strength and performance properties of aromatic polyesters and LDPE. To reduce cost AACs are often blended with TPS. Fossil fuel-based, AACs are biodegradable and compostable. ACCs fully biodegrade to carbon dioxide, water and biomass. (Muller R-J, et al 2001).

2.4.8.i. PHBH

Poly-hydroxybutyrate-co-polyhydroxyhexanoates (PHBHs) resins are derived from carbon sources such as sucrose, fatty acids or molasses via a fermentation process. They possess barrier properties as ethylene vinyl alcohol. PHBH polymer film manufactured by casting or blowing methods has costs comparable to traditional materials such as EVOH. PHBH resins biodegrade under aerobic as well as anaerobic conditions, and are digestible in hot water under alkaline conditions. (Kobayashi G, et al 1994).

2.4.8.j. POLYLACTIDE

PLA degrades to form lactic acid which is normally present in the body. PGA can also be broken down by certain enzymes. (Middleton JC, et al 1999). The rate of degradation is determined by configurational structure, copolymer ratio, crystallinity, molecular weight, morphology, stresses, and amount of residual monomer, porosity and site of implantation. (Koelling AS, et al 1997). PLA-PGA copolymers can be used in bone repair applications. (Athanasiou KA, et al 1998;Athanasiou KA, Schmitz JB, et al 1998). Implants with considerable size may result in high local acid concentrations. (Agrawal CM, et al 1995,Agrawal CM, et al 1997)

2.4.8.k. POLYLACTONE

PCL is a semi crystalline polymer with a glass transition temperature of about -60°C. The polymer has a low melting temperature (59 to 64°C) and is compatible with a range of other polymers. PCL degrades at a much lower rate that PLA. Poly (caprolactone) is prepared by the ring-opening polymerization of the cyclic monomer ε-caprolactone. Catalysts such as stannous octoate are used to catalyse the polymerization and low molecular weights alcohols can be used as initiator which also can be used to control the molecular weight of the polymer. PCL with an initial average molecular weight of 50,000 takes about three years for complete degradation *in-vitro*. The rate of hydrolysis can be altered by copolymerisation with other lactones. A copolymer of caprolactone and valerolactone degrades more readily. Copolymers of ε-caprolactone with dl-lactide show more rapid degradation rates. PCL is considered a non-toxic and a tissue compatible material. (Deniz K Armani 2000).

2.4.9 POLYORTHOESTERS

Poly(orthoester)s (POE) are suitable for orthopaedic applications. With the addition of lactide segments as part of the polymer structure, tunable degradation times ranging from 15 to hundreds of days can be achieved. The degradation of the lactide segments produces carboxylic acids, which catalyze the degradation of the orthoester. (Heller J, Barr J, et al 2002).

2.4.10 POLYPHOSPHAZENE

The polyphosphazenes consist of several hundred different polymers with the general structure. The polymer contains phosphorous nitrogen chains. They are readily hydrolyzed to give phosphoric acid and ammonia derivatives. Most polyphosphazenes are biostable, Specific side groups such as amino acid esters, glucosyl, glyceyl, lactate, or imidazolyl units make polyphosphazenes biodegradable. Hydrolysis of the polymer leads to free side group units, phosphate and ammonia due to backbone degradation. (Qui LY, Zhu KJ 2000).

2.4.11 POLYSACCARIDES

They are starch and cellulose derivatives in plastics or as water-soluble polymers. These polymers are composed of D-Glycopyranoside repeating thousands of units. Starch is poly (1,4-2-D-Glucopyranoside) and cellulose is poly (1,4-B-D-Glucopyranoside). The structure control biodegradation rates and properties of the polymers. Complex carbohydrates like microbially produced xanthan, curdlan, pullulan, hylauranic acid alginates, carageenan and guar are accepted biodegradable polymers. Xanthan is the prominent microbial polysaccharide and finds use in the food industry. It is also used as a thickener in many industrial applications. (Mark et al).

2.4.12 POLYUREAS

Polyureas prepared from lysine esters with 1, 6 hexane diisocyanate are readily degradable and is used in polymer drug application. The polyester urea from phenylamine containing hydrophobic benzyl group is readily hydrolyzed while unsubstituted polyester urea from glyline is not affected. (Santini J T et al 1999).

2.4.13 PROTEINS

They must be used as found in nature because they are not soluble or fusible without decomposition. (Tchmutin I. et al 2004). They are widely used as fibers e.g. wool, silk, gelatin (collagen). The structure of proteins is an extended chain of amino acid joined through amide linkages that are readily degraded by enzymes, particularly protease. (Saha N. et al 2003.

2.4.14 PUR

Polyester based polyurethanes are more susceptible to degradation than those derived from polyether diols. (Gunatillake PA, et al 2001, Hirt TD, et al 1996). As the flexibility of polyurethane increases, their susceptibility towards biodegradability increases. Polyamide urethanes prepared from amino alcohols are easily degraded by substilin. They have excellent mechanical properties and good biocompatibility. (Lamba NMK, et al 1998). They are used in the fabrication of medical implants such as cardiac pacemakers and vascular grafts. (De Groot JH, 1996). The toxicity of degradation products for PUR derived from the diisocyanate is a major problem. Polyethylene oxide (PEO) based polyetherurethane (PEU) are weaker but PCL based materials are relatively strong. (Zislis T et al 1989). No results on the degradation of these polyurethanes are known. In an artificial skin composed of polylactide/ polyurethane mixtures PU was non-degradable. (Bruin P, et al 1988)

2.4.15 STARCH

Starch is a linear polymer (polysaccaride) made up of repeating glucose groups linked by glucosidic linkages in the 1-4 carbon positions. The length of the starch chains will vary with plant source but in general the average length is between 500 and 2 000 glucose units. (Safari B., 2004). There are two major molecules in starch - amylose and amylopectin. The alpha linkage of amylose starch allows it to be flexible and digestible. Starch is made thermoplastic at elevated temperature in the presence of water as a plasticizer, allowing melt processing alone or in blends with other thermoplastic. Water lowers the melt transition temperature of starch so that processing can be done well below the degradation temperature. (Abd-Aziz, S. 2002)

2.4.16 STARCH BLENDS

The most important commercial application is the blending of PE with starch in presence or absebce of other additives. (Ahamed, N.T., et al 1996) The starch -PE are compatibilized with:

◊Ethylene acrylic acid copolymer

◊Ethylene vinyl alcohol polymers

◊Hydroxyacids

◊Urethanes

◊Polyamides

◊Polyvinyls

◊Cellulose acetate

◊Alkyds

◊Polycaprolactone

Starch-based biodegradable plastics have starch contents ranging from 10% - 90%. Crops such as corn (maize), wheat or potatoes can be used. Starch content must exceed 60% for significant material. (Bikiaris D et al 1998). At lower starch contents (less than 60%) the starch particles act as weak links in the plastic matrix and are sites for biological attack. This allows the polymer matrix to disintegrate into small fragments, but not for the entire polymer structure to actually bio-degrade. There are several categories of biodegradable starch-based polymers including:

a. Thermoplastic starch products;
b. Starch synthetic aliphatic polyester blends;
c. Starch PBS/PBSA polyester blends; and
d. Starch PVOH Blends.

2.4.16.a. THERMOPLASTIC STARCH PRODUCTS

Thermoplastic starch biodegradable plastics (TPS) have a starch (amylose) content greater than 70% and are based on gelatinised vegetable starch, and with the use of specific plasticizing solvents, can produce thermoplastic materials with good performance properties and inherent biodegradability. Starch is typically plasticised, destructured, and/or blended with other materials to form useful mechanical properties. Importantly, such TPS compounds can be processed on existing plastics fabrication equipment. (Dr Stephan P. Weeks 2001).

2.4.16.b. STARCH SYNTHETIC ALIPHATIC POLYESTER BLENDS

Blends of biodegradable synthetic aliphatic polyesters and starch are often used to produce high quality sheets and films for packaging by flat-film extrusion using chill-roll casting or by blown film methods since it is difficult to cast films from 100% starch in a melted state. Approximately 50% of the synthetic polyester can be replaced with natural polymers such as starch leading to a significant reduction in cost. (Lim, S.W.; et al 1999). Furthermore, the polyesters can be modified by incorporating a functional group capable of reacting with natural starch polymers.

2.4.16.c. STARCH AND PBS/PBSA POLYESTER BLENDS

A small amount (5% by weight) of compatibiliser (maleic anhydride functionalized polyester) can be added to impart phase stability to starch and PBS/PBSA polyester blends. At higher starch content (>60%), such sheets become brittle hence plasticizers are added to reduce the brittleness and improve flexibility. (Mani R., et al 1998).

2.4.16.d. STARCH-PVOH BLENDS

PVOH is readily water soluble. The starch-PVOH blends are degraded via hydrolysis and biodegradation of the sugar molecules. (P. A. Fowler, et al 2007).

2.4.17 TYROSINE DERIVED POLYCARBONATE

Tyrosine-based polycarbonates possess three potentially hydrolysable bonds: amide, carbonate and ester. The carbonate group hydrolyzes at a faster rate than the ester group, and the amide bond is not labile. The hydrolysis of the carbonate groups yields two alcohols and carbon dioxide, the problem of acid bursting seen in polyesters. By variation of the structure of the pendant R group, polymers with different mechanical properties, degradation rates and cellular response can be prepared. (Tangpasuthadol V, et al part- I 2000a, Part-II 2000b, Pathiraja A. Gunatillake et al 2003).

2.4.18 VINYL POLYMERS: PVAl, PVAc, EVOH

Their biodegradation requires an oxidation process and most of the biodegradable vinyl polymers contain an easily oxidisable functional group. To improve biodegradability of vinyl polymers, catalysts are added to promote their oxidation or photo degradation or both. Incorporation of photosensitive groups like ketones into the polymers is also attempted. (Westhoff R.P., et al 1974).

2.4.18.a. POLYVINYL ALCOHOL:

It is the most readily biodegradable of vinyl polymers. It is readily degraded in wastewater activated sludge. The initial step involves the enzymatic oxidation of the secondary alcohol groups in PVAL to ketone groups. Hydrolysis of ketone groups results in chain cleavage. Bacterial strain, such as pseudomonas, flavobacterium and azetobacter are effective in degrading PVAL. (Alexy , et al 2003) PVOH is a readily biodegradable, water soluble polymer. Conventional PVOH cannot be processed by traditional extrusion technologies because it decomposes at its melting point of 230°C. Even partially hydrolysed grades, which melt at 180-190□C, undergo some decomposition during melt processing. (Chiellini E, et al 2003). New grades of PVOH incorporating an internal plasticiser are extrudable and possess water solubility. PVOH does not biodegrade, but simply dissolves in water. Biodegradation of PVOH in soil is expected be very slow. (P. A. Fowler, et al 2007)

2.4.18.b. POLYVINYL ACETATE:

PVAL is obtained from hydrolysis of polyvinyl acetate. Controlled hydrolysis of PVAc followed by oxidation provides degradation material having a wide range of properties and degradability. PVAc undergoes slow biodegradation in soil burial tests. The weight loss increases with the acetate content. (P. A. Fowler, et al 2007)

2.4.18.c. ETHYLENE VINYL ALCOHOL (EVOH)

EVOH is water-soluble synthetic plastic, and is used as an oxygen barrier layer in multilayer film packaging. The high cost of EVOH is a significant barrier. (P. A. Fowler, et al 2007)

2.4.19 PE

Fungal and bacterial growth tests indicate that polyethylene and other high molecular weight carbon chain polymers do not support growth. (Ohtake, Y., Kobayashi, 1998). Anomalous results were observed when plasticizers or low molecular weight impurities were added. Branching of hydrocarbon chains limits biodegradation. There is an increase in biodegradation with lower molecular weight. The biodegradation process in PE can be accelerated with surfactants or an oxidation process.

2.4.20 MODIFIED PE

2.4.20.a. LDPE MIXED WITH ACYLATED CORN STARCH

The modified corn starch by acetylation reaction mixed with LDPE in 5, 10 and 20 percent. Under different condition of biodegradable process such as 15, 30 watt ultraviolet exposures, normal sunlight exposure and landfill application, it was found that LDPE compound mixed with the acetylation corn starch give better degradation than LDPE but it also give much less mechanical property , compare with the same percentage of corn starch . The 20 percent acetylation corn starch mixed with LDPE showed the highest degradation but not acceptable mechanical property while the 10 percent acetylation corn starch mixed with LDPE showed the degradation under every test condition and acceptation mechanical property. (F.J Rodriquez-Gonzalez, et al 1997).

2.4.20.b. LDPE MIXED WITH STARCH

Starch, can be processed into thermoplastic materials in presence of plasticizers and under the action of heat and shear. Poor water resistance and low strength are limiting factors. (Evangelista R.L., et al

1991).Starch blended with aliphatic polyesters has mechanical properties that are close to those of traditional plastics such as polyethylene and polystyrene. (Chandra R., et al 1997).

2.4.21 PHOTOBIODEGRADABLE PLASTICS

Photodegradable plastics are thermoplastic synthetic polymers into which have been incorporated light-sensitive chemical additives or copolymers for the purposes of weakening the bonds of the polymer in the presence of ultraviolet radiation. Photodegradable plastics become weak and brittle when exposed to sunlight for prolonged periods. Photosensitizes used include diketones, ferrocene derivatives (aminoalkyferrocene) and carbonyl-containing species. Some times catalytic metal salts or chelates are added to initiate the breakdown process. (Austin R.G., 1994).

2.4.22 CONTROLLED DEGRADATION ADDITIVE MASTER BATCHES

Additives that impart controlled degradation behavior to conventional thermoplastics, as well as to inherently biodegradable plastics, are becoming a popular strategy due to price competition. Such additives are known as prodegradant concentrates, and are generally based on catalytic transition metal compounds such as cobalt stearate or manganese stearate. The additive is typically used at levels of 1-3% and leads to additional costs of between 10-35% over that of polyethylene. Polyethylene containing 3% of the additive is claimed to degrade to a 95% weight loss after 4 weeks at 60°C. Such environmentally degradable plastics are not biodegradable but are 'bioerodable'. Polymers initially oxidize chemically to lower the molecular weights and become brittle to form fragments. (Kiatkamjornwong S., et al 2001). The fragments are then ingested slowly by microorganisms, ultimately leaving carbon dioxide, water and biomass.

2.4.23 BIODEGRADABLE PACKAGING POLYMERS

LDPE, HDPE, PP, and PS are blended with natural biodegradable products like starch. (Nathan A. Baker 2005). Compatibilizers, such as maleic anhydride-grafted polyethylene and polystyrene, are also made. (Ibeh, Christopher C. 2004).

2.4.24 THERMOPLASTICS FROM LOW QUALITY WOOD

Low-quality Wood or waste wood is chemically modified, such as by cyanoethylation and polymer grafting via isocyanate-mediation, to impart thermo plasticity so that it can be molded into useful products. (E. Sjöström, 1993).

2.5 EARLIER STUDIES ON BIODEGRADATION:

2.5.1 POLYMERS CONTAINING VARYING AMOUNT OF STARCH

The studies were conducted on thin films of various polymers that contained varying amounts of starch. Some microorganisms utilize starch, as a nutrient source and secrete enzymes which break the polymer. PE films containing starch resulted only in the biodegradation of starch. (Larry Krupp and William Jewell 1992)

2.5.2 BIODEGRADABLE BLENDS BASED ON SWEET POTATO STARCH

Biodegradable polymer blends composed of polyethylene and sweet potato starch were developed in 10, 20, and 50% starch weight compositions. (Arvanitoyannis H., et al 1998). The initial granular structure of starch is maintained after SEM micrographs indicate good dispersion representing good adhesion between starch and PE. (Kim M. 2003). DSC and X-Ray results indicate that the melting temperature and degree of crystallinity of the polyethylene remains constant as the starch content increases. (Van Soest, et al 1994). Mechanical testing show that modulus increases with starch content, strain decreases with starch content, and ultimate strength remains constant. (Kim M., et al 2002). Thus, the starch can be added up to 50%, with improved biodegradability without adverse affects on the blend. (D'Juanna Pattersonl et al 2004).

2.5.3 STARCH-BASED BIODEGRADABLE BLENDS: MORPHOLOGY AND INTERFACE PROPERTIES

Plasticized wheat starch blended with biodegradable polyesters [polyesteramide, poly (ε-caprolactone), poly(lactic acid), poly(butylene succinate adipate) and poly(butylene adipate terephthalate)] exhibit variable polar characteristics. (Pedrosa, A. G., et al 2005). The compatibility of these blends varies with formulation. (Raghavan D., et al 2001). Blend structures from SEM show either a dispersed structure or a co-continuous morphology. (Emmanuelle Schwachl and Luc Ave´ rous 2004).

2.5.4 STUDY OF DEGRADATION AND MECHANICAL PROPERTIES OF LDPE MIXED WITH ACETYLATED CORN STARCH

The biodegradation and mechanical property of LDPE that mixed with modified corn starch at 5, 10 and 20 percent. It was found that LDPE with corn starch give better degradation but has much less mechanical property. (Manuchehr Nikazarl, et al 2005). The 20 percent acetylation corn starch mixed with LDPE showed the highest degradation but not acceptable mechanical property while the 10 percent acetylation corn starch mixed with LDPE showed the degradation under every test condition and acceptation mechanical property. (Lee S.J., et al 1999).

2.5.5 MODIFICATION OF STARCH BY BLENDING WITH ALIPHATIC POLYESTERS

The biodegradable rates of blends of starch and aliphatic polyesters can be controlled to a certain extent depending on the constitutions of blends, and the mechanical properties of blends are close to those of traditional plastics such as polyethylene and polystyrene. The reduction of their sensitivity to humidity makes these materials suitable for the production of biodegradable films, injection-molded items, and foams. (Jane J., et al 1990).

2.5.6 DEGRADABLE PLASTIC FILMS FOR HORTICULTURAL CROPS PRODUCTION.

The silver/black bio/photo-degradable PE films containing 20% starch degraded after 56 ,83 , 38, and 33 days when they were mulched in fall(October,1991), winter(December,1991), spring(April,1992) and summer (August,1992), respectively. (Shaw-rong Yang et al). The more starch incorporated, the faster the films degraded. No difference was observed in yield in 6 consecutive years. The same results were also obtained in another trial on cantaloupe and paddy rice for 4 consecutive years. Six pieces (each 10cm¡Ñ10cm) of Bioplastics, Bioflex and Green choice biodegradable films were buried in a 8-inch clay pot. Then head lettuce was planted in the pots. The weight losses for Bioflex, Bioplastics and Green choice were 58.4%, 47.9% and 11.3%, respectively after 40 days.

2.5.7 BIODEGRADATION OF AN AGED COMPOSITION OF POLYETHYLENE WITH SYNTHETIC POLYESTER

The extent of abiotic degradation of LDPE modified with a low content (20%) of Bionelle polyester is studied. The microscopic fungi penicillium funiculosum, collected from a rubbish dump, was used for the biodegradation of the films. Photodegradation was induced by UV radiation in the range 250 - 400 nm, and thermal degradation at 50°C temperatures. The extent of degradation was assessed by loss of mass, mechanical strength, surface morphology, and infrared spectra. The results indicate that the addition of the polyester makes the polyethylene more sensitive to the action of abiotic degradation. (S. Łabużek, et al 2006).

2.5.8 THE CHARACTERIZATION OF BIODEGRADABLE POLYBUTYLENE SUCCINATE/STARCH BLENDS USING HDPE-G-ACRYLIC ACID AS A COMPATIBILIZER

Blends of polybutylene succinate, (PBSU) and starch with 5 phr compatibiliser HDPE-g-acrylic acid are assessed for properties. Some disruption of the crystal structure of PBSU occurs with the introduction of starch. A decrease in the melting temperature was also noted with increasing amounts of starch. A slight increase in tensile strength was observed when the compatibiliser was incorporated in the blends. A visible growth of microorganisms, at high concentrations of starch was seen. The rate of biodegradation was assessed based on the decrease in tensile strength during 4 weeks of soil burial. The weight loss increased with increasing treatment times and with starch content during extended soil burial. (Lai S M; Wu C S; Liao H T 2006)

2.5.9 BIODEGRADATION OF POLYETHYLENE BY THE THERMOPHILIC BACTERIUM BREVIBACILLUS BORSTELENSIS

A thermophilic bacterium Brevibaccillus borstelensis strain 707 (isolated from soil) utilized branched LDPE as the sole carbon source and degraded it. Maximal biodegradation was obtained in combination with photo-oxidation, which showed that carbonyl residues formed by photo-oxidation play a role in biodegradation. (Hadad, D., et al 2005). The study demonstrates that PE that is considered to be inert, can be biodegradable if it is subjected to a right microbial strain in a right biological system.

2.5.10 TENSILE PROPERTIES OF EXTRUDED CORN PROTEIN LOW-DENSITY POLYETHYLENE FILMS

Tensile strength, percent elongation at break, and elastic modulus of the films extruded from powder blends of corn zein or corn gluten meal (CGM) with low-density polyethylene were measured. The tensile strength decreased with zein addition. The tensile property reduces with the increase in contents of biological material (CGM or zein). Films containing CGM exhibited significantly lower tensile properties than those containing zein. (Thomas J. Herald et al 2002)

2.5.11 BIODEGRADABLE FILMS FROM MANNANS

Films were prepared from mannans with varying chemical structure. Various mannans used were: 1. galactomannans from guar beens 2. galactomannans from locust beans 3. glucomannan from konjac tubers, and 4. galactoglucomannan from spruce wood. (I.C.M. Dea, et al *1975*). Mannans with least substituted galactose formed strongest and most flexible films having Elongation at break. Konjac glucomannan produced films with the highest tensile strength. (L.H. Cheng, et al 2002). The tensile strength of the best galactomannan films was half that of films from konjac glucomannan. Increase in galactose substitution decreased the tensile strength of galactomannan films. The mechanical properties of galactomannan films improved with the reduction of the molecular weight up to a certain point, after which the strength decreased significantly. Spruce galactoglucomannan with low molecular weight formed films with low tensile strength and elongation at break although it has low galactose substitution. Increasing the amount of plasticizer increased the elongation at break but decreased the tensile strength of mannan films. There was no appreciable difference in mechanical properties between films plasticized with glycerol or sorbitol, but the glass transition temperature was lower for films containing glycerol. Films from konjac glucomannan were better oxygen barriers than films from spruce galactoglucomannan. (Kirsi Mikkonen, et al)

2.5.12 AN INVESTIGATION INTO THE AGING OF BIODEGRADABLE STARCH BASED PLASTICS

Different samples were subjected to aging for four weeks under extremes of humidity and temperature, and also a standard condition. (Thakore IM. et al 2001). The high temperature sample would not blow into film at all and the low humidity sample was difficult to blow, resulting in a homogenous film with approximately one third of the tensile strength of the model film. This indicates that a loss of water from the pellets greatly reduced the quality of the film. (Oriana Finkelstein 2000)

2.5.13 STUDIES ON BIODEGRADABLE POLY (HEXANO-6-LACTONE) FIBERS.

Poly (hexano-6-lactone) (PCL^2) ®bers were degraded under environmental conditions, including soil burial, seawater exposure, and activated sludge exposure. The extent of degradation was examined by weight loss, loss of mechanical properties, such a tensile strength and ultimate elongation decreases, and visual observations by scanning electron microscopy.

The degradation pro®le of the PCL ®ber depends on both the environmental conditions and the ®ne structure of the ®ber. The half-degradation times of drawn PCL mono®laments (28065mm) are 30±40, 120±150 and 15±30 days for soil burial, activated sludge exposure, and seawater exposure, respectively. The microbial degradability was decreased with increasing crystallinity by drawing, and with increasing diameter of the ®ber. (M. Mochizuki et al 1999. part 2, T. Hayashi et al 2002 part 3).

2.5.14 Polyethylene Biodegradation By A Developed Penicillium-Bacillus Biofilm

It was reported that polyethylene are susceptible to degradation by fungi. After a period of burial the carbonyl absorption band for LDPE extending from 1625 to 1850 cm, indicating various types of oxidation products formed during the biodegradation of polyethylene is in agreement with the biodegradation mechanism of polyethylene. (Gamini Seneviratne et al 2006)In polyethylene an auto oxidizable fatty acid ester generate peroxides which chemically attack the bonds in the polymer molecules reducing the molecular chains to a level where they can be consumed by microorganisms. Other mechanisms which play significant role are physical damage due to the microorganisms, biochemical effects from the extra cellular materials produced by the activity of microorganism. Moreover the rate of degradation is affected by environmental factors such as moisture, temperature and biological activity. Degradation of polyethylene was indicated by loss of weight and tensile strength.

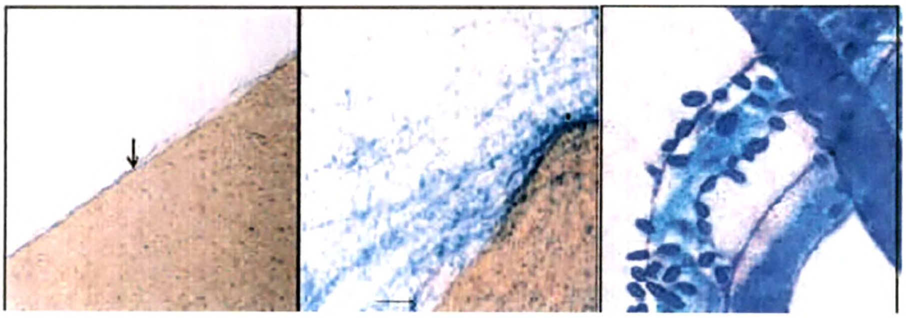

Figure: 2.2 Bio film formations from colonization of fungal filaments

2.6 PATENT LITERATURE:

2.6.1. Blends of biodegradable thermoplastic oxyalkanoyl polymer, a naturally occurring biodegradable product, filler and plastic additive

United States Patent 3931068

Inventors:

Chinnaswamy, Rangaswamy (Lincoln, NE, US)Hanna, Milford A. (Lincoln, NE, US)

Blends of biodegradable thermoplastic oxyalkanoyl polymer, e.g., epsilon-caprolactone polymer, and naturally occurring biodegradable product, e.g., tree bark are useful in the production of shaped articles such as mulch film, containers, package containersetc.

2.6.2. Biodegradable polymers

United States Patent 5496895

Inventors:

Kawabata, Nariyoshi (Osaka, JP)Kohsaka, Mutsumi (Moriyama, JP) Kurooka, Teruya (Fujiidera, JP)

Starch and a non-biodegradable polymer like PS, PUR, PE, PP, or PC are blended with oxidizing agent and treated under heat, pressure and reagents to break the polymers. Plastic and starch (15 - 80%) and oxidizing agent are processed in an extruder

2.6.3. Biodegradable polymer

United States Patent 20030118692

Inventors:

Wang, Yadong (Somerville, MA, US)Ameer, Guillermo (Chicago, IL, S) Langer, Robert (Newton, MA, US)

A condensation polymer of glycerol and a diacid is made. The polymer is used to construct tissue engineering. The polymer can also be used for different medical and non-medical applications.

2.6.4. Biodegradable polymer

United States Patent 20040242732

Inventors:

Yu, Long (Victoria, AU) Coombs, Stephen (Queensland, AU) Christie, Gregor Bruce Yeo (Victoria, AU)

A biodegradable polymer is composed of 8 -80% by weight of a starch modified with hydroxyalkyl or modified by reaction with an anhydride of a dicarboxylic acid. The hydroxypropylated high amylose starch is made from 0 to 87.9% of starch, 4 to 11% by weight of a water soluble polymer like PVAl, PVAc and copolymers of EVOH having a melting point compatible with the molten starch components, 0 to 20% by weight of a polyol plasticiser, (glycerol), 0.1 to 1.5% by weight of fatty acid or salt (stearic acid) and, 0 to 12% added water. The polymers are suitable as biodegradable rigid sheet or flexible film materials for use in packaging foodstuffs.

2.6.5. Biodegradable polymer

United States Patent 20040122135

Inventors:Halley, Peter (QLD, AU)McGlashan, Stewart (QLD, AU) Gralton, John (QLD, AU)

A biodegradable polymer is made from 20 to 60% of starch and/or a modified starch, 8 to 22% of starch plasticisers and processing agents, 30 to 70% biodegradable aliphatic polyesters and 1 to 10% of a layered silicate clay mineral. The silicate mineral is an organoclay. The polymers also include the usual additives like 0 to 20% by weight of a polyol plasticiser, 0.1 to 1.5% by weight of fatty acid or salt or a destructing agent like urea and/or urea derivatives, and from 0 to 12% by weight of added water. The polyester may be modified by reaction with maleic anhydride.

2.6.6. Biodegradable cationic polymer

United States Patent 7179874

Inventors:

Shau, Min-Da (Kaohsiung, TW) Cherng, Jong-Yuh (Tainan, TW) Yang, Tsung-Fu (Changhua, TW) Chin, Wei-Kuo (Taipei, TW)

The biodegradable cationic polymer has amino groups in the backbone and side chains, self-assembles cationic complexes with nucleic acids, and delivers nucleic acids into a cell by endocytosis. It has very low cytotoxicity.

2.6.7. Phosphate based biodegradable polymers

United States Patent 20020155092

Inventors:

Leong, Kam (Ellicott City, MD, US) Jie, Wen (Baltimore, MD, US) Zhuo, Ren-Xi (Wuhan, CN) Mao, Hai-Quan (Singapore, SG)

The biodegradable polymers contain repeat units derived from cyclic phosphate, lactide or caprolactone monomers.

2.6.8. Phosphate based biodegradable polymers

United States Patent 6805876

Inventors:

Leong, Kam W. (Ellicott City, MD, US) Jie, Wen (Baltimore, MD, US) Zhuo, Ren-Xi (Wuhan, CN) Mao, Hai-Quan (Singapore, SG)

The biodegradable polymers contain repeat units derived from cyclic phosphate, lactide or caprolactone monomers.

2.6.9. Polymer dispersion with improved biodegradability

United States Patent 20020035181

Inventors:

Willner, Kurt (Reutlingen, DE, US) Fischer, Thomas (Beuren, DE, US)

The polymer dispersion contains esters of natural or synthetic origin, saturated mono- or polyunsaturated carboxylic acids, linear or branched saturated or mono- or polyunsaturated alcohols are used. Dicarboxylic acid residues are subject to single and/or double esterification. Carboxylic acid residues are derived from citric acid which may be esterified by reaction with acetic anhydride.The alcohol component is derived from glycerol, diglycerol, triglycerol or tetraglycerol including the polyglycerols, respectively in the form of mixed esters or esters of a single acid. The formulation comprises mixtures of synthetic esters with mineral oil, hydrocarbons and/or paraffins. The polymer is derived from monomers having an ethylenically unsaturated double bond, like unsaturated carboxylic acids,(acrylic acid, methacrylic acid, maleic acid or itaconic acid)

2.6.10. Biodegradable film

United States Patent 20050163944

Inventors:

Isshiki, Nobuyuki (Tochigi, JP) Odajima, Shingo (Tochigi, JP) Goto, Minoru (Tochigi, JP)

A biodegradable film with a biodegradable wax as moisture barrier layer is placed between two biodegradable resin layers. The biodegradable polymer is a heat-resistant natural rubber or polyisoprene.

2.6.11. Biodegradable cationic polymers

United States Patent 20060258751

Inventors:

Zhao, Gang (Vista, CA, US) Fu, Xiaoli (Vista, CA, US) Yu, Lei (Carlsbad, CA, US)

Polymers is made from polyethylenimine, (biodegradable) and a hydrophobic group are useful for the delivery of bioactive agents to cells.

2.6.12. Biodegradable polymer compositions

United States Patent 4999417

Inventors:

Domb, Abraham J. (Baltimore, MD, US)

Biodegradable polyanhydrides or polyester compositions are based on amino acids. The compositions may be used as carriers for drugs or as a drug source itself. The polymers are prepared from amino acids which are modified to include an additional carboxylic acid group.

2.6.13. Biodegradable polymers

United States Patent 20030224497

Inventors:

Warner, John C. (Norwood, MA, US)Morelli, Alessandra (Quincy, MA, US)Ku, Man Ching (Braintree, MA, US)

The methods of solubilizing and recycling of a photoreactive polymers using irradiation,are mentioned. These polymers have many applications in disposable consumer products such as beverage bottles, eating utensils and diapers.

2.6.14. Biodegradable polymer systems

United States Patent 20040242722

Inventors:

Rose, John (York, GB) Hardwick, Steven (York, GB)

The rate of degradation of polymers and polymer blends containing (poly) lactic acid can be increased and controlled by adding up to 10% (typically less than 1%) by weight of lauric acid or a derivative of the anhydride.

2.6.15. Composite biodegradable polymer scaffold

United States Patent 20030082808

Inventors:

Guan, Limin (Toronto, CA, US) Holy, Chantal E. (Toronto, CA, US) Shoichet, Molly S. (Toronto, CA, US) Davies, John E. (Toronto, CA, US)

A polymer scaffold is provided comprising an extensively interconnected macroporous network having a diameter in a range of 0.5-3.5 mm, and in a range of about 1.0-2.0 mm. The polymer scaffold is prepared by particulate leaching and phase inversion. The polymer scaffold is used in tissue engineering.

2.6.16. Biodegradable polymer compositions

United States Patent 5516825

Inventors:

Montador, Henry J. (Cleveland, GB) Webb, Andrew (Cleveland, GB)

Biodegradable polyesters derived from hydroxy alkenoic a plasticised with an esterified hydroxycarboxylic acid having at least three ester groups. Some of the hydroxy groups are esterified with a carboxylic acid and some of the carboxy groups are esterified with an alcohol and/or phenol.

2.6.17. Biodegradable polymers of lactones

United States Patent 4379138

Inventors:

Pitt, Colin G. (Durham, NC, US) Schindler, Anton E. (Durham, NC, US)

Homopolymers and copolymers of lactones are prepared by ring-opening polymerization of a mixture of lactones which includes a monolactone, such as caprolactone, and a dilactone, such as bis-2,2-(-caprolacton-4)propane, which is capable of forming crosslinks. The resulting polymers range from tough and partially crystalline to amorphous, elastomeric materials, depending on the monomer composition and proportions. Different degrees of permeability and rates of biodegradation can also be achieved. They are useful for the controlled delivery of medicinal agents and as surgical aids and temporary artificial biomaterials such as skin substitutes and burn dressings.

2.6.18. Biodegradable coatings of ionomer polymer

United States Patent 4741956

Inventors:

Thaler, Warren A. (Flemington, NJ, US) Manalastas, Pacifico V. (Edison, NJ, US) Drake, Evelyn N. (Lebanon, NJ, US) Lundberg, Robert D. (Bridgewater, NJ, US)

A polymeric composite made from urea; and a coating of sulfonated polymer. The sulfonate groups is neutralized with a polycaprolactone polymer which is an alkyl, cycloalkyl or aryl group

2.6.19. Method of making porous biodegradable polymers

United States Patent 6673286

Inventors:

Shih, Hsi-Hsin (Taichung, TW) Lee, Kuang-Rong (Hsinchu, TW) Lai, Huey-Min (Hsinchu, TW) Tsai, Chin-Chin (Taichung, TW) Chang, Yuan-Chia (Taipei, TW)

A biodegradable polymer and a solvent are placed in a chamber. A supercritical fluid is added to the chamber and the chamber is maintained at a predetermined temperature for a sufficient period of time so that the supercritical fluid dissolves into the biodegradable polymer with the help of the solvent. The supercritical fluid and the solvent are vented by reducing the pressure in the chamber. Thus a porous biodegradable polymer is obtained.

2.6.20. Biodegradable polymer blend

United States Patent 20030187149

Inventors:

Schmidt, Harald (Emmerich, DE, US) Friedek, Wolfgang (Bedburg-Hau, DE, US) Vogt, Petra (Rees, DE, US)

A biodegradable polymeric blend can be produced by extrusion. It contains aromatic polyester and aromatic and/or aliphatic blocks. 10% w. of this polymeric blend with aromatic polyester contains aliphatic polyester based on hydroxycarboxylic acid and/or lactone. This polymeric blend do not include plastifying agent.

2.6.21. Biodegradable fishhook

United States Patent 5890316

Inventors:

Rodgers, Jack (Santa Barbara, CA, US) Petit, Michael G. (Santa Barbara, CA, US)

A fishhook disintegrates upon standing for prolonged periods of time in an aqueous environment. The fishhook comprises of a biodegradable polymeric hook-shaped structure with a metal tip fixed to provide a sharp piercing element. The polymer biodegrades when exposed to the chemical environment of the fish's tissue. Sometimes the entire fishhook is fabricated from a biodegradable polymer such as polylactide or polyglycolide or a copolymer thereof.

2.6.22. Methods of making functional biodegradable polymers

United States Patent 20030232929

Inventors:

Huang, Yanbin (Roswell, GA, US) Kim, Jaeho (Roswell, GA, US)

A method to modify biodegradable polymers using direct reaction of a biodegradable polymer in a vinyl monomer in the presence of initiators is claimed. The initiator can be free radical initiators, heat, ionic initiators, UV irradiation, ionizing irradiation and other high energy irradiation. The biodegradable polymer can be polycaprolactone, poly(lactic acid), poly(glycolic acid) and poly(lactic-co-glycolic acid). The vinyl monomers can be acrylates, methacrylates.

2.6.23. Biodegradable netting

United States Patent 20050183329

Inventors:

Cederblad, Hans O. (Minnetonka, MN, US) Misukanis, Keith E. (Eagan, MN, US) Hakanson, Christopher P. (Woodbury, MN, US) Thoen, Andrew J. (Harris, MN, US)

The biodegradable extruded netting comprises a plurality of interconnected strands with 10% strands comprising a biodegradable composition comprising polylactic acid polymer and biodegradable plasticizer.

2.6.24. Biodegradable bag

United States Patent 20040241359

Inventors:

Miksic, Boris A. (North Oaks, MN, US) Vela, Pasko (Lino Lakes, MN, US) Berg, Robert (Richfield, MN, US) Boyle, Robert (Oakdale, MN, US)

A biodegradable bags formed from biodegradable film includes the blended product of polylactic acid and a suitable biodegradable polymeric resin. The blended product includes from about 5% to about 50% by weight polylactic acid.

2.6.25. Biodegradable polymer compositions and shrink films

United States Patent 5866634

Inventors:

Tokushige, Yuji (Ibaraki-ken, JP) Ooura, Makoto (Ibaraki-ken, JP) Nakamura, Norio (Tokyo, JP)Ueda, Shuhei (Ibaraki-ken, JP)

The biodegradable polymer made from a mixture of polylactic acids, glycol/aliphatic dicarboxylic acid copolymers and polycaprolactones has higher elongation at break, Izod impact strength and mold releasing ability. A biodegradable shrink film has excellent transparency, strength, flexibility, mold releasing ability and shrink ability.

2.6.26. Biodegradable and breathable polymer film

United States Patent 20050112350

Inventors:

Ning, Xin (Alpharetta, GA, US)

A film which is biodegradable and breathable comprises of 30% - 70% by weight of a biodegradable copolyester and 70% - 30% by weight of a filler. The film is stretched in either a monoaxial or biaxial direction to increase void formation and achieve a water vapor transmission rate (WVTR) greater than 1900 grams per square meter per 24 hours. The aliphatic/aromatic acids copolyester and calcium carbonate filler is used. The film is suitable for use in disposable breathable products such as personal care products, absorbent products, health care products, bandages and medical fabrics.

2.6.27 Biodegradable cards

United States Patent 6096431

Inventors:

Matsudaira, Nagahisa (Saitama, JP) Imai, Toshibumi (Saitama, JP) Sen, Li Han (Saitama, JP) Taniguchi, Masayuki (Tokyo, JP)

A biaxially oriented sheet of a biodegradable thermoplastic PLA resin is used as a structural material for a supporting substrate of a biodegradable card. The average molecular weight of PLA is from 10,000 to 1,000,000.

2.6.28. Biodegradable film

United States Patent 20050182204

Inventors:

Otome, Shigeo (Kyoto-shi, JP) Iwai, Kunihiro (Osaka-shi, JP) Sohgawa, Yow-hei (Tondabayashi-shi, JP)

A biodegradable film containing 30 to 100% by mass of polyethylene succinate-based polymer hardly pollutes the environment even when being discarded. It has excellent transparency, adequate flexibility required in a film.

2.6.29. Compositions of biodegradable natural and synthetic polymers

United States Patent 5321064

Inventors:

Vaidya, Utpal R. (Inver Grove Heights, MN, US) Bhattacharya, Mrinal (Vadnais Heights, MN, US)

A biodegradable polymer composition is prepared by blending of a synthetic polymer having functional groups of naturally occurring biodegradable polymer such as a carbohydrate or protein compound. During reactive blending, the synthetic polymer undergoes a chemical reaction with the biodegradable natural polymer resulting in covalent and physical bonding between the two polymers. Biodegradable polymer is suitable for molding various articles.

2.6.30. Biodegradable starch-based polymer compositions

United States Patent 5449708

Inventors:

Schiltz, David C. (Columbus, OH, US)

Aqueous lubricant material is added to a homogeneous mixture of starch, an ethylene acrylic acid co-polymer, and a salt of stearic acid are premixed. An increase in temperature gelatinizes the starch and melts the co-polymer. Excess moisture is removed under reduced pressure and a plastic material is extruded.

2.6.31. Biodegradable copolymer, a biodegradable polymer composition, a biodegradable article, and a preparation process thereof

United States Patent 5834567

Inventors:

Yasuda, Hajime (Hiroshima-ken, JP)

A biodegradable copolymer having a number average molecular weight ranging from 1,000 to 1,000,000 consisting 5-99% by mol of *E*-caprolactone or valerolactone structural units and 95-1% by mol of oxetane structural units combined in the state of a block, and containing an organic aluminum-based Lewis acid is independently selected from a substituted group.

2.6.32. Biodegradable polymer compositions and shrink films

United States Patent 5726220

Inventors:

Tokushige, Yuji (Ibaraki-ken, JP) Nakamura, Norio (Tokyo, JP) Tanifuji, Yoichi (Tokyo, JP) Ueda, Shuhei (Ibaraki-ken, JP)

Polylactic compositions possess excellent mold releasability upon processing. It has improved elongation at break, impact strength and transparency. A shrink film made from the material decomposes under the natural environment and has excellent transparency, flexibility, shrinkability and mold releasability. A biodegradable polymer composition comprises of 100 parts by weight of polylactic acid and 5-70 parts by weight of EVA. Additives consisting of 0.05-5 parts by weight of a lubricant, 1-50 parts by weight of plasticizer, 0.5 - 5 parts by weight of thermal stabilizer and 0.05 - 5 parts by weight of mold releasing agent.

2.6.33. Methods of making functional biodegradable polymers

United States Patent 7037983

Inventors:

Huang, Yanbin (Roswell, GA, US) Kim, Jaeho (Roswell, GA, US)

A method to modify biodegradable polymers with the direct reaction of a biodegradable polymer in a vinyl monomer in the presence of initiators is carried out. The initiator is free radical initiators, heat, ionic initiators, UV irradiation, ionizing irradiation and other high energy irradiation. Biodegradable polymers used are polycaprolactone, poly (lactic acid), poly (glycolic acid) and poly (lactic-co-glycolic acid). The vinyl monomers used are acrylates, methacrylates. The ratio of the vinyl monomer to the biodegradable polymer is about 30:70 -70:30. The reaction occurs at room temperature or at an elevated temperature.

2.6.34. Fibers comprising starch and biodegradable polymers

United States Patent 20030109605 United States Patent 20020188041 United States Patent 6946506 United States Patent 6890872

Inventors:

Bond, Eric Bryan (Maineville, OH, US)Autran, Jean-Philippe Marie (Wyoming, OH,US) MacKey, Larry Neil (Fairfield, OH, US) Noda, Isao (Fairfield, OH, US) O'Donnell, Hugh Joseph (Cincinnati, OH, US)

Environmentally degradable fibers are produced by melt spinning process. The composition comprises of destructurized starch(5-85%), a biodegradable thermoplastic polymer(5-90%) having a molecular weight of 30,000 g/mol to less than 500,000 g/mol(PLA, diacid/diol aliphatic polyesters, aliphatic/aromatic copolyesters), and a plasticizer(2-70%).

Environmentally degradable finely attenuated fibers produced by melt spinning a composition comprising destructurized starch, a biodegradable thermoplastic polymer, and a plasticizer are disclosed. The present invention is also directed to highly attenuated fibers containing thermoplastic polymer microfibrils which are formed within the starch matrix of the finely attenuated fiber. Nonwoven webs and disposable articles comprising the highly attenuated fibers are also disclosed.

2.6.35. Biodegradable bag

United States Patent 6984426, United States Patent 20060121220

Inventors:

Miksic, Boris A. (North Oaks, MN, US)Vela, Pasko (Lino Lakes, MN, US) Berg, Robert (Richfield, MN, US) Boyle, Robert (Oakdale, MN, US)

A biodegradable bag formed from biodegradable film formed from a blown film extrusion process includes the blended product of polylactic acid (5-50% by weight), balance aliphatic aromatic copolyester resin and a biodegradable polymeric resin.

2.6.36. Thermoplastic photodegradable and biodegradable polymer blend

United States Patent 5763518

Inventors:

Gnatowski, Marek (Coquitlam, CA, US)Koutsandreas, Andy (Vancouver, CA, US)Foster, Terry (Victoria, CA, US) Fookes, David (New Westminster, CA, US)

A photodegradable and fully biodegradable plastic material,molded using conventional molding techniques having good physical and mechanical properties includes a blend of 10-500 parts by weight polycaprolactone per 100 parts by weight of polyisoprene resins2-6 parts of stearic/palmitic fatty acid and 0.03-0.20 parts of an organic peroxide (1,1,-di-(t-butylperoxy)-3,3,5-trimethylcyclohexane) per 100 parts of total polycaprolactone and polyisoprene in a weight ratio of up to 4:1. Additives may be casein, antioxidants, dyes, fillers, or vulcanized vegetable oils, coupling agents, fragrances, blowing agents, antistatic agents, fire retardants and pigments. The material biodegrades in soil and sea water environments. All blend ingredients are completely decomposed by microorganisms. Polyisoprene is a natural rubber obtained in a large variety of plant species or is synthetic. Polycaprolactone is a synthetic polymer resin known to be decomposed by microorganisms.

2.6.37. Biodegradable mixtures of polyphoshazene and other polymers

United States Patent 6077916

Inventors:

Laurencin, Cato (Elkins Park, PA, US)Allcock, Harry (State College, PA, US) Ibim, Sobrasua (Forrest Park, GA, US) Ambrosio, Archel (Philadelphia, PA, US) Kwon, Michael (Narberth, PA, US)

Biodegradable polyphosphazenes (ethyl glycinato-substituted polyphosphazene (PPHOS) with p-methylphenoxy as co-substituent) are combined with at least one other polymer (PLGA). The side groups and composition of the polyphosphazenes are used to determine the rate and extent of degradation, and mechanical properties. These are useful in biomedical applications, controlled drug delivery, tissue regeneration and environmental applications. The polyphosphazenes contain hydrophobic side groups, such as p-methylphenoxy and other aromatic groups, and groups which impart hydrolytic instability, such as amino acid alkyl esters, and degrade by bulk/surface erosion.

2.6.38. Biodegradable film

United States Patent 6156929

Inventors:

Chandler, Christophe (Woodbury, MN, US)Miksic, Boris A. (North Oaks, MN, US) Ahlbrecht, Arthur H. (Stillwater, MN, US)urrier, Jude (Maplewood, MN, US)

Biodegradable polyesters of polylactic acid and polycaprolactone are blended and can be processed by the conventional plastics processing techniques. with a particulate vapor phase corrosion inhibitor like amine salts, ammonium benzoate, triazole derivatives, tall oil imidazolines, alkali metal molybdates, alkali dibasic acid salts, in an amount between 1% - 3% by weight of the polymeric resin.

2.6.39. Biodegradable card

United States Patent 6372331

Inventors:

Terada, Shigenori (Shiga, JP) Takagi, Jun (Tokyo, JP)

A biodegradable card with laminated over-layers having a major component of 60-100 wt % of a polylactic acid and 40-0 wt % of a biodegradable aliphatic polyester. Both sides of a core layer is 40-90 wt % of a polylactic acid and 60-10 wt % of a biodegradable aliphatic polyester

2.6.40. Biodegradable film

United States Patent 20020052445

Inventors:

Terada, Shigenori (Shiga, JP) Takagi, Jun (Tokyo, JP)

A film having high flexibility and transparency is degradable in natural environment. It comprises of a polymer of polylactic acid family and aliphatic polyester having a number-average molecular weight of 10000 to 150000 other than polylactic acid in a weight ratio of from 70:30 to 20:80. The tensile modulus of film is not more than 250 kg/mm and a light transmittance of that is not less than 65%.

2.6.41. Biodegradable plastics

United States Patent 20040249065

Inventors:

Schilling, Christopher H. (Midland, MI, US) Karpovich, David S. (Gagetown, MI, US) Tomasik, Piotr (Cracow, PL)

A biodegradable plastic from natural materials containing polysaccharides and oligosaccharides is made by treating the polysaccharide-containing or oligosaccharide-containing materials with a basic aqueous solution. The mixture is treated with a modifying material to create an anionic product, and then is contacted with the anionic product with proteins to produce the biodegradable plastic material The natural material can be starchy materials, cellulosic materials, lignocellulosic materials, hemicellulosic materials, plant gum containing materials, polysaccharide-containing materials and oligosaccharide-containing materials, plant tubers, wheat seeds, shells of seeds, stems, roots,leaves of plants, fruit, fruit skins, wood, tree branches, tree bark, straw grass, distiller, dry grain sugar, beet pulp, cellulose pulp, paper, waste cotton, linen, vegetables and vegetable skins. The protein can be soy protein isolate, casein separated from milk, casein dispersed in milk, whey protein isolate, whey protein, potato protein, ovalbumin, animal albumins, blood protein, and molasses raffinate.

2.6.42. Biodegradable polyester and natural polymer laminates

United States Patent 6040063

Inventors:

Doane, William M. (Morton, IL, US) Lawton, Jr., John W. (Chillicothe, IL, US) Shogren, Randal (Peoria, IL, US)

A self-supporting structure is formed of natural polymer (gelatinized starch and a hydroxy-functional polyol.). It has a self-adherent, moisture resistant hydroxy-functional polyester on the structure surface. The self-supporting structure is a starch and polyvinyl alcohol blend in an expanded form. The articles typically do not delaminate even when soaked in water, and are biodegradable.

2.6.43. Biodegradable bag

United States Patent 6960374

Inventors:

Terada, Shigenori (Shiga, JP) Takagi, Jun (Tokyo, JP)

The biodegradable bag can be heat-sealed at low temperature, does not develop corrugation, has transparency, and has degradability in the natural environment. The polylactic acid-family polymer film and an aliphatic polyester (1, 4-butanediol, succinic acid, and adipic acid) film are heat-sealed so that the biaxially oriented film with polylactic acid-family polymer as an outer layer is manufactured.

2.6.44. Biodegradable bags and processes for making such biodegradable bags

United States Patent 5679421

Inventors:

Brinton, Jr., William F.

Biodegradable bags are formed out of two-ply sheet materials. The outer ply is of craft paper and an inner ply is of biodegradable thermoplastic material (polyvinyl alcohol, hydroxyethylcellulose polymer, polyethylene glycol polymer, polycaprolactone, polylactic acid, hydroxybutyrate polymer, hydroxyvalerate polymer, and a copolymer of hydroxybutyrate and hydroxyvalerate). The two-ply sheets are formed and connected together with the use of biodegradable adhesives (starch). The sheets are laminated and joined together, using heat-sealing procedures.

2.6.45. Biodegradable polyesters

United States Patent 6120895

Inventors:

Kowitz, Christoph (Weinheim, DE, US) Bauer, Peter (Ludwigshafen, DE, US) Beimborn, Dieter Bernhard (Weisenheim, DE, US) Bruchmann, BerndFreinsheim, DE, US) Faller, Uwe (Frankenthal, DE, US) Laun, Martin (Ludwigshafen, DE, US) Pagga, Udo (Ludwigshafen, DE, US) Pipper, Gunter (Bad Durkheim, DE, US) Warzelhan, Volker (Weisenheim, DE, US)

Biodegradable polyesters 95-99.99 mol % of polyester containing an acid component of 20-95 mol % aliphatic or cycloaliphatic dicarboxylic acid or its ester-forming derivative, 5-80 mol % of aromatic dicarboxylic acid or its ester-forming derivative, dihydroxy compound, amino alcohol or their mixtures, 0.01-5 mol % of a mixture comprising mono-, bi-, tri-, tetra- and higher-nuclear isocyanurates or mixtures of the isocyanurates, molding compositions comprising said polyesters.

2.6.46. Biodegradable polyurethanes

United States Patent 6221997

Inventors:

Woodhouse, Kimberly AnnSkarja, Gary Alan

A biodegradable polyurethane material having a molecular weight of 25,000 to 140,000 containing one amino acid group (L-phenylalanine and L-lysine) in its backbone is formed by reaction of aliphatic diol, a polyethylene oxide and polycaprolactone diol based polyol, a lysine-based diisocyanate and a chain extender. The biological agent is an endogenous enzyme. It is useful as an artificial skin, a wound dressing or a tissue engineering scaffold.

2.7 SUMMARY OF EARLIER STUDIES ON BIODEGRADATION:

The biodegradation of synthetic polymers is sharply divided between those suggesting that microbiological attack can only occur if polymers could be degraded to extremely short chain lengths, and those suggesting that synthetic polymers can also be metabolised at relatively high molecular weights. (Ungtae Lee et al 1991) The microbiological process which lead to the destruction of natural polymers such as starch, cellulose and proteins during exposure to soil are well understood. However, for the commercialized synthetic polymers, there are conflicting claims regarding their sensitivity to microbiological attack. A variety of environmental factors such as oxygen, temperature, sunlight, water, stress, living organisms and pollutants may affect the degradation of polymer. Therefore, it is important from the viewpoint of soil microbiology to determine the biodegradability of plastics and microorganisms responsible for it in each soil condition for reaching the general conclusion on its biodegradability.

A degradation of polymers may proceed by one or more mechanisms, including microbial degradation in which microorganisms such as fungi and bacteria consume the material. Earlier studies on biodegradation and the patented work shows that the experimental work on biodegradable polymers carried out so far focuses on:

◊Naturally biodegradable polymers
◊Water soluble polymers
◊Starch blends/additives
◊Naturally biodegradable polymers as additives in conventional non degradable polymers
◊Naturally biodegradable polymers with plasticizers
◊Biodegradation of conventional non degradable polymers with selected microorganisms

Experiments using plasticizer as the modifying agent of the polymer that are not biodegradable are still not carried out (Anthony L. Pometto Iii et al 1992). The use of plasticizers that are susceptible to microorganisms and are not in commercial use today is the base of the present study.

2.8 LIMITATIONS OF COMMERCIAL BIODEGRADABLE POLYMERS:

◊Most of the biodegradable polymers are not commercially viable due to their higher cost.

◊Major applications of biodegradable polymers are in medical field.

◊Biodegradable polymers are too unstable for long term industrial use. (Williams CT, et al 1998).

◊There is a public opposition against genetically modified foods.

◊Manufacture of biodegradable polymers consumes more energy than the conventional polymers.

◊Mode of the degradation is mainly by hydrolysis which in turn pollutes the water.

◊Migration of plastic degradation by-products such as residual pigments, catalyst residues and isocyanate via run-off and leachate from landfills and composting facilities to groundwater and surface water bodies is resulted.

◊Trauma and death of marine species resulting from only partial or slow degradation of biodegradable plastic products in marine environments is caused.

◊They increase the littering as the people believe that biodegradable plastics will disappear quickly.

◊It increase the soil and crop degradation resulting from the use of compost that may have unacceptably high organic and or metal contaminants derived from biodegradable plastic residuals, additives and modifiers such as coupling agents, plasticizers, fillers, catalysts, dyes and pigments.

◊They do not disappear completely and leave visible trace and toxic residues. (Tayler M.S., et al 1994)

◊They do not possess the strength and storage comparable to that of the conventional polymers.

Search for a cost effective biodegradable plastic carry bags, because of its immense impact on society and environment is still on. If the search fails, the alternative, as some of the countries in the world and some of the states in India, seems to ban the use of the product and go back to paper bags which is in effect equally environmentally viable because one needs large quantity of natural cellulose sources (like bamboo/soft wood/hard wood) to produce paper, in the first place.